Improving digestibility of cattle waste by thermobarical treatment: Lab-scale experiments and assessment of full-scale model application

Dissertation

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Dipl.-Ing. (FH) Jörn Budde

Gutachterin: Prof. Dr. Annette Prochnow
Gutachter: Prof. Dr. Jerry D. Murphy
Ph.D. Henrik Bjarne Møller

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Abstract

Hydrolysis and digestibility of cattle waste as feedstock for anaerobic digestion were improved by thermobarical treatment in lab-scale experiments. The effects of this improvement on greenhouse gas emissions, energy balance and economic benefit was assessed in a full-scale model application.

Thermobarical treatment temperatures in lab-scale experiments were 140 to 220°C in 20 K steps for a 5-minute duration. Methane yields could be increased by up to 58 % at a treatment temperature of 180°C. At 220°C, the abundance of inhibitors and other non-digestible substances led to lower methane yields than those obtained from untreated material. In an extended analysis, it could be demonstrated that there is a functional correlation between the methane yields after 30 days and the formation rate and methane yield in the acceleration phase. It could be proved in a regression of these correlation values that the optimum treatment temperature is 164°C and that the minimum treatment temperature should be above 115°C.

The theoretical application of a full-scale model was used for assessing energy balance and greenhouse gas emissions following an LCA approach according to ISO 14044 (2006) as well as economy. A model device for thermobarical treatment has been suggested for and theoretically integrated in a biogas plant. The assessment considered the replacement of maize silage as feedstock with liquid and / or solid cattle waste. The integration of thermobarical pretreatment is beneficial for raw material with high organic dry matter content that needs pretreatment to be suitable for anaerobic digestion: Solid cattle waste revealed very short payback times, e.g. 9 months for energy, 3 months for greenhouse gases, and 3 years 3 months for economic amortization, whereas, in contrast, liquid cattle waste did not perform positive replacement effects in this analysis.

Zusammenfassung

Im Laborversuch konnte der positive Einfluss einer thermobarischen Vorbehandlung auf die Hydrolysier- und Vergärbarkeit von Rinderfestmist und Rindergülle nachgewiesen werden. Die Laborergebnisse wurden innerhalb eines theoretischen Modells in den Praxismaßstab übertragen, um den Einfluss auf Treibhausgasemissionen, Energiebilanz und Ökonomie zu bewerten.

Die Vorbehandlungstemperaturen im Labor lagen zwischen 140 und 220°C in Schritten von 20 K und einer Vorbehandlungszeit von jeweils 5 Minuten. Die höchste Methanmehrausbeute von 58 % konnte bei einer Temperatur von 180°C ermittelt werden. Das Auftreten von Inhibitoren und nicht vergärbaren Bestandteilen führte bei einer Aufbereitungstemperatur von 220°C zu Methanausbeuten, die geringer waren als die des unaufbereiteten Einsatzstoffes. In einer erweiterten Analyse konnte ein funktioneller Zusammenhang zwischen der Methanausbeute nach 30 Tagen und der Methanbildungsrate und -ausbeute während der Beschleunigungsphase gezeigt werden. Mittels einer Regressionsanalyse der so ermittelten Werte wurde nachgewiesen, dass die optimale Aufbereitungstemperatur 164°C ist und die minimale größer als 115°C zu sein hat.

Treibhausgasemissionen und Energiebilanz wurden im Rahmen einer Ökobilanz nach ISO 14044 (2006) ermittelt, sowie eine Kosten-Nutzen-Analyse durchgeführt. Dazu wurde eine Anlage zur thermobarischen Vorbehandlung entwickelt und innerhalb eines Modells in eine Biogasanlage integriert. Weiterhin wurde in diesem Modell Maissilage durch Rinderfestmist und / oder Rindergülle als Einsatzstoff ersetzt. Rinderfestmist, ein Einsatzstoff mit hohem organischen Trockenmassegehalt, der ohne Vorbehandlung nicht einsetzbar wäre, erreichte eine energetische Amortisationszeit von 9 Monaten, eine Vermeidung in Höhe der während der Herstellung emittierten Treibhausgase innerhalb von 3 Monaten und eine ökonomische Amortisationszeit von 3 Jahren 3 Monaten, wohingegen Rindergülle keine positiven Effekte zeigte.

1. Introduction

1.1. Motivation

Anaerobic digestion is a mature and proven technology providing a versatile renewable energy carrier (Browne & Murphy, 2013). The growing number of biogas installations and the rising demand for higher methane output have led to an increasing request for sustainable and cost-competitive provision of bioenergy resources and hence for a shift from liquid animal waste to solid energy crops and residues from agricultural production (Plöchl et al., 2009). Therefore, the biogas sector is not only encouraged to deploy new and untapped biomass resources (Zhang et al., 2013a), but also to use advanced and innovative technologies to improve biogas production and process efficiency as well as to increase cost effectiveness (Appels et al., 2008; Ward et al., 2008).

Livestock waste represents a huge, still only marginally exploited potential as feedstock for conversion processes. At present, 152 million tons of pig and cattle waste, comprising 120 million tons of liquid and 32 million tons of solid waste, are available in Germany annually (Schultheiß et al., 2010). Owing to low dry matter content, livestock waste is not appropriate for combustion without previous energy-intensive drying. By contrast with biomasses rich in sugars and oils, it is much more difficult to convert lignocellulose-rich biomasses such as bedding straw enclosed in the wet matrix of livestock waste into biogas. Lignocellulose and especially lignin are either not or only slightly degradable under anaerobic conditions (Grabber, 2005; Ward et al., 2008). Furthermore, lignocellulosic feedstock tends to float and agglomerate to an almost irreversible floating layer in the digester. Thus, the complex structure of lignocelluloses requires appropriate pretreatment to enable hydrolysis and hence efficient fragmentation of less digestible material for the subsequent biogas process.

1.2. Requirements on feedstock properties for anaerobic digestion

Anaerobic digestion is common for different branches of industry like food industry or waste management as well as agriculture. Therefore, many diverse kinds of feedstock like food residues, sewage sludge, different agricultural biomasses (annual as well as perennial crops) as well as lignocellulosic residues from other industries are applied. In addition, remains of a lot of other branches have come to focus, at least theoretically or in lab-scale, like for example from forestry. This thesis is focusing on agricultural biomass, residues, and wastes as feedstock for anaerobic digestion.

Plant species and variety as well as growing conditions primarily determine the chemical composition and the morphology of the biomass. These characteristics are strongly affected by all steps of the entire supply chain, as there are e.g. cutting, chopping, drying or ensiling. Regarding agricultural residues, the utilization of the particular biomass before it is

considered as feedstock for anaerobic digestion – e.g. if it is used as forage or litter – is to be considered as well.

On a macroscopic level, the size and intactness of the particles determine the available surface area as well as the microbial accessibility of more easily digestible constituents that are often enclosed by an (almost) indigestible hull (Carlsson et al., 2012). On a microscopic or molecular level, biomasses and biomass residues differ mainly in the share of four main constituents as there are water, lignin, cellulose, and hemicellulose. High moisture content, low crystallinity and degree of polymerization of the cellulose, and low lignin content indicate appropriate plant characteristics for anaerobic digestion (Zheng et al., 2014).

Beside the inherent plant properties, processing or pretreatment can result in the formation of products that may inhibit or destroy the microorganisms directly (necrotoxins) or indirectly by disturbing the environment necessary for optimal microorganism growth (Hendriks & Zeeman, 2009).

The aim of any treatment is therefore to improve the characteristics named above with the lignocellulosic complex being the main target. Figure 1 exemplarily shows a generalized secondary cell wall structure of grass for lignocellulosic structures. Cellulose (ribbon-like shape) and hemicellulose (cylindrical and triangular prismatic shapes) are embedded in lignin (dots). The hydrogen bond between cellulose and hemicellulose is depicted as square dots (Bidlack et al., 1992).

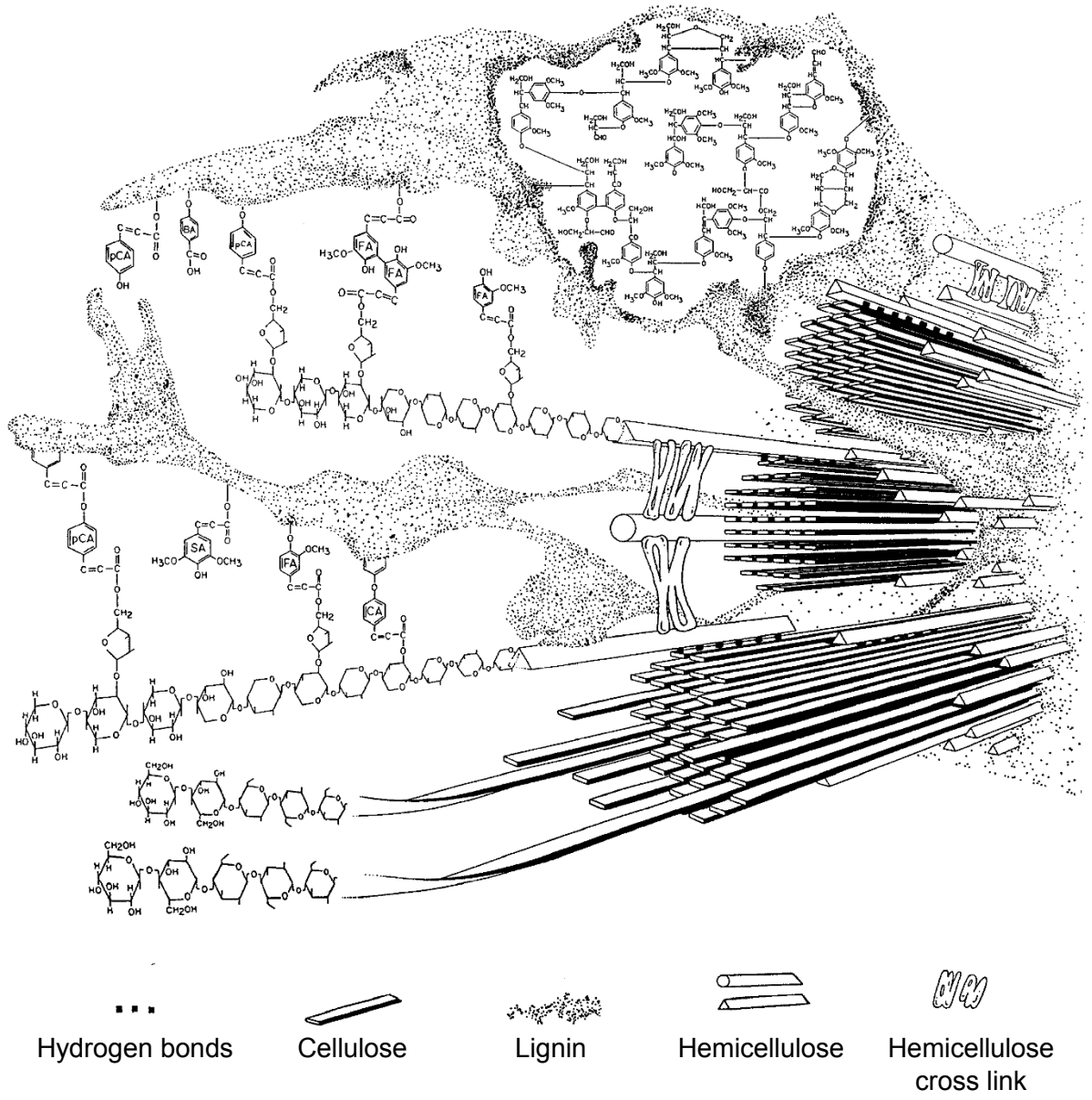

Figure 1: Lignocellulosic complex (Bidlack et al., 1992, p. 55)

As hydrolysis is the limiting step in anaerobic digestion (Vavilin et al., 1996), any pretreatment able to enhance the biological hydrolysis therefore positively influences the digestibility. Various authors reviewed the topic of pretreatment options (see section 1.3.) and feedstock properties for anaerobic digestion, gave literature surveys, and compiled pretreatment methods and associated effects on feedstock properties comprehensively (Carlsson et al., 2012; Hendriks & Zeeman, 2009; Zheng et al., 2014). These reviews also comprise the literature used for sections 1.3.1. and 1.3.2.

1.3. Pretreatment options – State of the art

1.3.1. Overview

In contrast to any kind of biorefinery process with high value added final products for material use, biogas or methane as final product of anaerobic digestion is currently used as energy carrier only. Therefore, a thorough pretreatment making the entire biomass available for the anaerobic microbial community is not only too cost-expensive but also and in particular not energetically efficient.

The description of effects caused by any kind of pretreatment is focused on the molecular level mainly as it is generally assumed that the alteration of chemical constituents – especially lignin, cellulose, and hemicellulose – due to pretreatment will be reflected by the (anaerobic) microbial decomposition of the biomass (section 1.2.).

There are various basic principles available for feedstock treatment. These principles are described in detail in the following section.

1.3.2. Basic principles

Physical treatment

The most elementary way of physical treatment is **mechanical treatment** in the form of milling, grinding, shredding, chopping, and similar. It leads to an augmentation of the vulnerable surface without substantial degradation of any part of the hemicellulosic complex.

Another elementary way is boiling in water. Boiling at temperatures higher than 100°C under saturated water vapor pressure is common. This process is called **thermobarical hydrolysis** or liquid hot water treatment. It leads to a much increased vulnerable surface area as well as to hydrolysis of cellulose and solubilization and depolymerization of hemicellulose and lignin. Thus, not only intracellular material is released for the hydrolysis by anaerobia through the disintegration but hydrolysis is also partially anticipated. Although water is a chemical reaction partner (e.g. autohydrolysis needs the presence of water), it is not regarded a chemical in this thesis.

Steam treatment is used for achieving the same effect as thermobarical hydrolysis but instead of liquid water, steam is used. The steam is not released quickly after treatment, whereby steam explosion is avoided.

Steam explosion of substrates is caused by a fast shift between a temperature of above 100°C combined with the saturated water vapor pressure (e.g. 1.01 bar at 100°C) and no pressure (respectively atmospheric pressure). If the pressure is decreased very fast, the intra- as well as extracellular water is evaporating immediately leading to explosion of the substrate. The same effect can be achieved by switching between atmospheric pressure and pressure lower than atmospheric pressure. At about 20 mbar water is boiling at room

temperature. This effect is known as cavitation from different machines with rotating parts of a high peripheral velocity in liquids. It can also be stimulated by ultrasonic radiation using sonotrodes.

There are a lot of **mixed forms** of physical treatment combining purely mechanical treatment with high temperature and/or pressure. For example, extruder and low or high pressure homogenizer combine mechanical treatment and steam explosion if used at ambient temperature and also thermobarical hydrolysis if higher temperatures are applied.

Biological treatment

Ensiling is one of the most commonly used methods for pretreating agricultural biomass. Biomass-inherent **bacterial communities** are decomposing carbohydrates and proteins under anaerobic conditions. Although biomass is rather ensiled for conservational purposes, the conversion of biomass constituents to easily available organic acids and alcohols is beneficial to subsequent anaerobic digestion as well.

Pretreatment by microbial communities or fungi (including yeasts) leads to decomposition of either cellulose and hemicellulose or lignin.

A well analyzed way of biological pretreatment of less digestible material is the application of isolated **enzymes** or enzyme mixtures. Enzymes like cellulases or hemicellulases are used for enhanced hydrolyzation of the respective constituents.

Chemical treatment

Depending on the chemicals used and the physical conditions, e.g. higher temperatures or pressure, a lot of different reactions can take place. Acid and dilute acid pretreatment are able to lead to the following effects:

- solubilization of cellulose, hemicellulose, and partly lignin,
- increase of the accessibility of the cellulose fraction,
- hydrolysis of cellulose and hemicellulose to monomers,
- further conversion of decomposition products to furfural, hydroxymethylfurfural, phenol, and others.

Alkaline pretreatment is able to lead to

- intracrystalline moisture expansion of cellulose and thus an augmentation of the vulnerable surface,
- solvation and saponification,
- disintegration of the lignin structure,
- solubilization of lignin and condensation of decomposition products,
- decrease in the degree of polymerization,

- alteration in the crystallinity of the cellulose,
- breaking down the links between the lignin and the carbohydrates.

Oxidative pretreatment is able to cause

- oxidative cleavage of aromatic nuclei,
- electrophilic substitutions,
- displacement of side chains,
- cleavage of alkyl aryl ether linkages,
- decomposition of hemicellulose and partly cellulose to monomers,
- further conversion of the decomposition products to organic acids,
- cleavage and oxidation of lignin,
- increase of the accessibility of the cellulose fraction.

1.3.3. Short review on lab-scale pretreatment

As mentioned in section 1.2., this thesis focuses on biomasses and residues derived from agriculture as well as on subsequent biomethanation. Therefore, this short review does not consider publications dealing with other resources of biomasses, like residues from forestry or algae nor municipal organic wastes or with differing subsequent conversion routes like alcoholic fermentation or aerobic degradation.

Mechanical treatment in lab-scale experiments is not regarded as pretreatment in the sense of this review if applied in order to homogenize or to reduce particle size to fit the experimental apparatus. Nevertheless, it is a kind of pre-pretreatment to the pretreatment to biomethanation the respective study is actually dealing with. The transferability of the results obtained in lab-scale experiments into practice is to be seen in consideration of all treatments applied to the raw material. Therefore, the respective lab-scale method is given in addition to the results obtained by applying the actual pretreatment in the following.

Physical pretreatment

Recently many studies have been published dealing with physical pretreatment. Most of these describe steam explosion or thermal or thermobarical pretreatment and rarely purely mechanical or ultrasonic pretreatment.

Bauer et al. (2009) investigated **steam explosion** of wheat straw as pretreatment for combined ethanol and methane production. Before steam explosion the wheat straw was pretreated by using an impact milling for achieving particle sizes between 0.5 and 1.0 mm. One (1) kg of wheat straw was mixed with 3 kg of water before steam explosion in a 15 liter reactor with steam injected at 20 bar, temperatures of 160, 180, and 200°C and retention

times of 10, 15, and 20 minutes. After steam explosion the methane potential was examined in batch anaerobic digestion tests.
Steam explosion, as conducted here, leads to an increase in methane yield of 14 % at 160°C for 10 minutes and in maximum 20 % at 180°C for 15 minutes. All other pretreatment variants also show an increased mean value but do not differ in a statistically significant way from untreated wheat straw.

Another study evaluated the effect of **steam explosion** on wheat straw as well but additionally used a mixture of wheat straw and cattle manure for subsequent anaerobic digestion tests (Risberg et al., 2013). The wheat straw was also milled before steam explosion but only until it passed a 10 mm sieve. 250 g per batch of that milled wheat straw were treated in a preheated 20 liter vessel at 210°C for 10 minutes. In contrast to other studies, the anaerobic digestion tests were conducted in 8 liter lab-scale continuous stirred-tank reactors in addition to batch anaerobic digestion tests, the first using several different digestion conditions.
Batch digestion tests of untreated and steam explosion treated wheat straw revealed a decrease in methane yield of 21 %. Semi-continuous digestion tests show an increase in methane productivity (in $l \cdot kg^{-1}$ $VS \cdot d^{-1}$) of 31 % in maximum at 37°C digester temperature and at lowest organic loading rate (OLR) tested, 2.5 g $VS \cdot l^{-1} \cdot d^{-1}$.

Ferreira et al. (2014a) also used **steam exploded** wheat straw as raw material for subsequent biomethanation. Before steam explosion at a temperature between 170 and 220°C and a treatment time between 1 and 15 minutes the straw was ground to particle sizes of 3 to 5 cm. One (1) kg of ground wheat straw was fed to a 30 liter reactor where the steam explosion took place. In the following, the pretreated material was investigated in batch anaerobic digestion tests.
Methane yields were increased for all pretreatment variants by 24 to 27 %. Optimal condition was found at a treatment temperature of 200°C and a treatment time of 5 minutes.

In another experiment, Ferreira et al. (2014b) treated the solid fraction from pig slurry, gained by centrifugation, with **steam explosion**. Steam explosion was conducted by feeding 250 g of pig manure to a preheated reactor of 2 liters where it was kept at temperatures between 120 and 180°C for 5 to 60 minutes. Treated and untreated slurry was afterwards digested in batch anaerobic digestion tests.
The methane yield of the solid fraction of pig slurry was increased by 107 % in maximum by steam explosion in this study. All treatment variants led to significantly higher methane yields in every case. In an advanced analysis the correlation between pretreatment time, pretreatment temperature, and methane yields was presented. A treatment at 170°C for 30 minutes was identified as optimum for separated solids from pig slurry.

Bauer et al. (2014) once again tested the impact of different **steam explosion** scenarios on late harvested hay from extensively cultivated grassland. Steam explosion was conducted by treating 300 g of hay in a 20 liter reactor for 5 to 15 minutes at temperatures between 160 and 220°C. After treatment the substrates were tested in batch anaerobic digestion tests.
The batch anaerobic digestion tests revealed increased as well as decreased methane yields, depending on treatment conditions. The highest increase in methane yield compared to untreated hay, 16 %, was gained at a treatment temperature of 175°C and treatment duration of 10 minutes. But most variants showed decreased biogas (and methane) yields at temperatures above 175°C, up to 27 % for variant 220°C / 10 minutes.

The effect of pretreating cow manure from slaughterhouse by **steam explosion** was investigated by Cano et al. (2014). The substrate was treated for 30 minutes at 170°C in a 2 liter reactor before batch anaerobic digestion tests.
The methane yield gained from this cow manure was increased by 29 % due to steam explosion pretreatment.

Bruni et al. (2010) investigated the effect of **steam pretreatment** on biofibers. The biofibers were gained from digestate from a biogas plant using a mixture of cow and pig manure, maize silage, and industrial by-products as feedstock. They were steam-treated in a 3 liter vessel at 180°C for 15 minutes without a fast pressure release after these 15 minutes that would have led to steam explosion. Methane potential was measured in batch anaerobic digestion tests at thermophilic conditions.
These treatment conditions led to an increase in methane yield of 29 % compared to untreated biofibers.

Mladenovska et al. (2006) **thermobarically treated** the solid fraction (600 µm mesh) of a mixture of cattle and swine manure at a temperature of 100 to 140°C for 20 or 40 minutes. After pretreatment the solids were separated from the liquid fraction by filtering before they were used as substrate for batch anaerobic digestion tests at thermophilic temperatures of 55°C for 80 days.
The treatment resulted in an increased methane yield between 9 % and 24 % or 10 % and 17 % for treatment times of 20 and 40 minutes, respectively, whereas best results were achieved at 100°C and a treatment time of 20 minutes.

The impact of **thermal pretreatment** on the anaerobic biodegradability of pig manure was analyzed by Carrère et al. (2009). The manure was pretreated in a 2 liter glass reactor at temperatures below 100°C and in a 900 ml reactor Zipperclave (Autoclave France) at temperatures higher than 100°C. Treatment times were 3 hours at 70 and 90°C and 20 minutes at temperatures between 135 and 190°C. Batch anaerobic digestion tests were

conducted for evaluating the methane potential. The pretreated manure was therefor mixed with the anaerobic sludge, oligo nutrients and buffer solutions.
The thermal pretreatment led to decreased methane yields for the 70°C treatment and the 135°C treatment (not statistically significant). The 90°C treatment led to a 12 % (not significant) increase in methane yield. From 150°C on, the methane yield increased with increasing temperature from 49 % higher than the untreated manure up to 64 % at a temperature of 190°C.

Dewatered pig manure was treated **thermobarically** by Rafique et al. (2010). 25 g of pig manure was treated in a closed vessel at laboratory scale at temperatures between 50 and 150°C for 1 hour. After this treatment methane yields were determined in batch anaerobic digestion tests for 29 days.
An increase of methane yield of 30 % was observed if dewatered pig manure is pretreated at 100°C for 1 hour.

Menardo et al. (2011) investigated the effect of **thermobarical pretreatment** of 3 different digestates from different biogas plants and raw solid swine manure on biomethanation. Treatment was conducted at 2 l autoclaves at 120°C for 30 minutes. The vessels were cooled down by releasing the pressure within 1 minute. Batch anaerobic digestion tests were conducted at mesophilic temperatures of 40°C and a digestion time of 56 days.
Depending on digestate origin the surplus in methane yield was -16 %, +12 %, and +117 %, respectively, the surplus in methane yield of solid swine manure was 170 %.

Cow and pig manure were **thermobarically treated** by Qiao et al. (2011). The manures were diluted by adding water before treatment at 170°C for 1 hour in 1 liter stainless steel vessels. Methane potential was determined in batch anaerobic digestion tests.
The thermal treatment led to a decrease in methane yield of 7 % in case of the cow manure and to an increase of 15 % for the pig manure compared to untreated manures.

Thermobarical treatment was applied to rice and wheat straw by Chandra et al. (2012a, 2012b). The straws were dried and ground to less than 1 mm before pretreatment. Twenty (20) gram of input materials were thermobarically treated at 200°C for 10 minutes. Prior to batch anaerobic digestion tests carried out at mesophilic temperatures (37°C) 5 % NaOH was added to maintain appropriate pH for anaerobic digestion.
Results differ between the types of straw: A 122 % surplus in methane yield was achieved within 40 days of batch anaerobic digestion test if rice straw was pretreated thermobarically whereas pretreating wheat straw led to a yield increased by 20 % only.

The effect of a **thermobarical pretreatment** on sugar beet pulp was investigated by Ziemiński et al. (2014). 100 g dry matter (DM) of sugar beet pulp were suspended in 300 ml distilled water prior to pretreatment in a 0.6 liter reactor for 20 minutes at temperatures between 120 and 200°C. Before anaerobic batch digestion tests the pH of pretreated substrates was adjusted to 7.2.
The thermobarical pretreatment led to significantly increased methane yields of between 49 and 76 % in each case. Highest increase was determined at a treatment temperature of 160°C.

Sugarcane press mud was **thermobarically pretreated** by López González et al. (2014) before anaerobic digestion. 100 g DM of air-dried sugarcane press mud was mixed with 500 g deionized water before pretreatment in a 0.6 liter reactor at 140 to 210°C for 2 to 23 minutes.
The pretreatment caused increased methane yields for all variants except the pretreatment at 200°C for 20 minutes. The increases were between 3 and 63 %. The optimum was at a temperature of 150°C and a treatment time of 20 minutes.

A 55 kW_{el} **twin-screw extruder** of company Lehmann Maschinenbau GmbH (Model MSZ B55e) was used for pretreating thirteen types of different biomasses as there are straw, grass, solid fractions from screw-pressed or flocculated and filtered manure obtained from both cow and pig manure collected from three commercial farms, and deep litter from a variety of sources (Hjorth, et al., 2011). Ten (10) liters of feedstock were extruded per batch. The outlet where the treated substrate was sampled was adjusted to maximum opening. For energetic assessment, the in- and outlet temperatures as well as the consumption of electric energy of the extruder were measured. After pretreatment the biogas yield was measured in batch anaerobic digestion tests.
The analysis showed an increase in methane yield in every case although not always statistically significant. After 90 days of batch anaerobic digestion test, the increase in methane yield was lower than after 28 days. The increase after 28 days was between 18 % (solid manure fraction) and 70 % (straw), after 90 days between 9 % (grass) and 28 % (deep litter). Energetic assessment shows that for pretreating a mass flow of 1.5 t fresh matter (FM) per hour between 4 and 10 $kWh_{el} \cdot t^{-1}$ FM is consumed. The net increase in electric energy due to pretreatment was found to be between 6 % (grass) and 26 % (deep litter) after 90 days. Furthermore, the authors determined from an extended analysis that extrusion is only effective on large particles and that the effect of extrusion is strongly dependent on the particular biomass used. They stated an accelerated degradation of slowly degradable compounds and a degradation of compounds that otherwise would not have been degradable due to extrusion.

Another pretreatment was conducted using a **Hollander beater** model Reina (Tedesco et al., 2014). This machine cut the substrates between blades and the grooves at the bed-plate, and it beat them while passing the space under the drum at high pressure and speed. Substrates used were seaweeds collected on-shore in Howth (Dublin, Ireland). Machine parameters modified for pretreatment of 2 kg seaweeds and 20 liters of water per batch were beating time (5 to 15 minutes) and the gap between the blades and the bed-plate (between 76 and 836 µm). Pretreated substrates were tested in batch anaerobic digestion tests for their biogas or methane potential. Three (3) different temperatures, 30, 40, and 50°C, were used for conducting the tests.
The maximal increase in methane yield determined was 53 % at a machine gap of 76 µm, a treatment time of 10 minutes, and a batch anaerobic digestion test at 50°C. The publication also presents a model of the correlation between pretreatment variant and temperature during batch anaerobic digestion test and methane yields before and after pretreatment. The model aims at minimizing pretreatment time and incubation temperature and at maximizing methane yield. It predicts the optimal treatment conditions with a beating time of 11 minutes, machine gap 76 µm, and biomethanation at 30°C. Corresponding to the model an increase of methane yield of 51 % is to be expected.

Elbeshbishy et al. (2011) examined the effect of **ultrasonic pretreatment** on hog manure for anaerobic digestion. Sonication was conducted by using 200 ml of hog manure and sonication pulses of 2 seconds on and 2 seconds off. Temperature was controlled at 30°C by using a water bath. Specific energy inputs into material were between 250 and 30,000. After pretreatment the methane potential was measured in batch anaerobic digestion tests. In an extended analysis, the impact on full-scale implementation was assessed (see section 1.3.4.).
Ultrasonication as conducted here leads to increased methane yields in every case. The increase ranged from 10.9 % to 28 %, whereas highest increase was observed at 500 $kJ \cdot kg^{-1}$ DM specific energy input. The methane production rate was increased as well: The variant with the highest methane yield reached the final (after 44 days) methane yield of the untreated variant after 19 days only.

Biological pretreatment

The study of Zhong (2011) dealing with biological pretreatment is on air-dried corn straw as raw material. Before biological pretreatment using **yeasts and cellulolytic bacteria** as microbial agents, the straw was pre-pretreated by being chopped with a paper chopper and being ground with a hammer mill to a final particle size of 5 to 10 mm. One (1) gram of ground straw was mixed with 10 ml distilled water and autoclaved at 121°C for 120 minutes. Autoclaving is to be regarded as pre-pretreatment as well. No information is given if the

autoclaving procedure was conducted for the control variant (straw ground only) as well. The mixture of raw materials and microbial agents was incubated between 0 to 20 days. For subsequent biochemical methane potential tests, the carbon-to-nitrogen ratio was adjusted using ammonium chloride, and for ensuring anaerobic conditions sodium sulfide was used in addition to gassing with nitrogen.
The batch anaerobic digestion tests revealed methane yields that increase with incubation time and are in general higher than the untreated variant. Methane yield increase is determined between 26.7 and 75.6 %.

Sugar beet pulp and spent hops powder were used for **enzymatic hydrolysis** for subsequent semi-continuous anaerobic digestion tests by Ziemiński et al. (2012). Sugar beet pulp was milled to an ultimate particle diameter of 0.25 cm prior to enzymatic hydrolysis. Different endoglucanases, xylanases, and pectinase at doses between 0.03 and 0.75 filter paper units per g DM were mixed with suspensions of sugar beet pulp and spent hops in water at a 10 % weight / volume DM ratio. Incubation proceeded at 50°C for 24 hours.
The effect of enzymatic hydrolysis on sugar beet pulp was much higher than on spent hops. The biogas volume per day increased by 19 % for sugar beet pulp and 13 % for spent hops compared to control variants.

López et al. (2013) investigated the effect of **fungal pretreatment** using ligninolytic fungus *Phanerochaete flavido-alba* on wood fiber, grass, corn stover and wheat straw. For pretreatment, 200 g of substrate were sterilized in 2 l flasks in autoclave at 121°C for 20 minutes before they were inoculated with 240 ml of a culture of fungus on growth medium at 30°C for 10 days. Digestion for determining the biogas yield took place in a solid state anaerobic digestion system through high-rate dry anaerobic batch fermentation. In a second test, the input materials were digested before and after inoculation with ligninolytic fungus.
In this study no effect on biogas yield was achieved through pretreatment, neither by the first variant nor by the second.

The effect of an **enzyme preparation** showing mainly pectinolytic activity with cellulase and hemicellulase as main side activities on maize or rye silage was published by Schimpf et al. (2013). Two (2) to 10 g silage were mixed with enzyme preparation in a ratio of 0.07 g enzyme preparation per kg of silage before anaerobic batch digestion tests were carried out for 65 days under mesophilic conditions.
Results obtained showed an increase in methane yield of 9.2 % for maize silage and of 6.3 % for rye silage after 35 days and of 15.3 % and 10.2 % after 65 days, respectively.

Suárez Quiñones et al. (2011) pretreated maize silage, rye grain silage, solid manure, and feed residues using a commercially available **enzyme preparation** before subsequent

continuous digestion tests. The respective substrate was mixed with the hydrolytic enzyme mixture in 250 ml stoppered Erlenmeyer flasks and kept for 3 hours at 40°C. Afterwards the substrate-enzyme-mixture was fed to the first of two mesophilic 10 liters reactors in series. The hydraulic retention time was between 80 and 90 days.
The methane yield was decreased in the case of feed-residues but increased for all other substrates tested. The increases presented are 3 % for solid cattle manure, 6 % for rye grain silage, 10 % for maize silage, up to 19 % for grass silage.

Suárez Quiñones et al. (2012) again used an **enzyme preparation** for pretreating maize silage, rye grain silage, solid manure, and feed residues. Three (3) different enzyme applications were tested: the use of inactivated enzymes, enzymes, and of enzymes and acetate buffer. In addition, the enzyme concentration, pretreatment temperatures, and pH-values were varied. Methane potential was tested in batch anaerobic digestion tests under mesophilic conditions (35°C).
Depending on feedstock and pretreatment variant the methane yield was increased up to 105 %. Maize silage (30 % increase in methane yield) and solid cattle manure (105 % increase) are variants displaying better results when enzymes were applied solely, whereas rye grain silage (+22 %), grass silage (+26 %), and feed residues (+58 %) showed highest increases when enzymes were applied in combination with acetate buffer.

Chemical pretreatment

The applicability of **sodium hydroxide treatment** as pretreatment for anaerobic digestion was analyzed by Zheng et al. (2009). Raw material used was corn stover chopped and ground until a particle size between 5 and 10 mm was reached. NaOH dosis was between 2 and 10 % based on dry matter of corn stover. The NaOH was dissolved in distilled water, mixed with the ground corn stover in 2 liter bottles and kept at ambient temperature (20 ± 2°C) for three days. In the following, the untreated and pretreated substrates were analyzed in batch anaerobic digestion tests for their methane potential. The carbon / nitrogen ratio of the mixture of inoculum and substrate was adjusted by adding a specific amount of ammonia chloride.
All treatment variants tested revealed higher methane yields of pretreated variants compared to untreated ones. In each case the highest increase was observed at dosages of less or equal than 4 % NaOH. Increases in methane yield were between 1.2 and 73.4 %.

Sodium hydroxide was added to rice and wheat straw by Chandra et al. (2012a, 2012b). The straws were dried and ground to less than 1 mm before pretreatment. Twenty (20) gram of input materials were mixed with 0.60 g powdered NaOH and kept for 5 days at 37°C prior to batch anaerobic digestion tests carried out at mesophilic temperatures (37°C).

Results differ between the types of straw: A 25 % surplus in methane yield was achieved within 20 days of batch anaerobic digestion tests if rice straw was pretreated chemically using NaOH whereas pretreating wheat straw led to a yield increased by 113 %.

Another **sodium hydroxide treatment** was presented by Sambusiti et al. (2013). Ensiled sorghum forage was air-dried and ground to a particle size of 0.5 mm before it was soaked in a sodium hydroxide solution of 10 g NaOH per 100 g DM in a 500 ml glass bottle. The initial DM concentration was 160 g $DM \cdot l^{-1}$, the pH of the sorghum suspension increased to 10 or higher. The bottle was kept at 40°C for 24 hours without stirring. After that treatment the methane potential was determined in semi-continuous anaerobic digestion tests.
Results show that alkaline pretreatment of sorghum silage increases the methane production yield by 25 % compared to that of untreated sorghum.

Zhang et al. (2013b) examined the impact of **sodium hydroxide treatment** on banana stem and swine manure. Banana stem was cut to a length of 1 cm and air-dried prior to wet-state pretreatment by the addition of NaOH with 2 %, 6 %, and 10 % (by weight) at 55°C for 54 hours. Swine manure was crushed after air-drying. Batch anaerobic digestion tests were conducted to determine the methane yields of treated and untreated substrates.
The variants treated with 2 and 6 % NaOH showed increased methane yields of 1 and 3 % respectively. Pretreated with 10 % NaOH methane yield was decreased by 2 %. All changes recorded were not statistically significant.

Wheat plants were used as substrate for **sodium hydroxide treatment** by Taherdanak & Zilouei (2014). The plants were air-dried and milled to particle sizes of less than 1 mm. The ratio of grains – consisting of 12 % w/w husks – to whole plant was 47 % w/w. Five (5) g on DM basis of these wheat plants were mixed with 95 g NaOH solution (8 % w/v) and stirred for 10 minutes at room temperature. Afterwards the mixture was incubated for 60 min at 0, 25, 50, 75 and 100°C, respectively. During incubation the mixture was stirred every 10 minutes. Prior to neutralization to pH 7 by washing with distilled water through vacuum filtration, the incubated mixtures were centrifuged. Methane yields were measured using batch anaerobic digestion tests.
The methane yields of pretreated variants were higher in all cases with the exception of the variant incubated at 0°C that showed a 25 % lower methane yield compared to untreated variant. The increases were between 5.3 and 47.5 %. An incubation temperature of 75°C was found to present optimal conditions. At this temperature, the formation rate was much increased as well: The variant incubated at 75°C reached the methane yield of the untreated variant at day 9, that is 21 days earlier than the untreated variant.

Two kinds of manure fibers were pretreated by **aqueous ammonia soaking** by Jurado et al. (2013). The first manure fiber was derived from raw swine manure by separation using a decanter centrifuge, the second from digested swine manure. Manure fibers were soaked in ammonia reagent (32 % w/w in ammonia) with a ratio of 10 ml reagent per 1 g DM in closed glass flasks for 1, 3, and 5 days at temperatures of 22 and 55°C respectively. Ten (10) ml water per g DM were added prior to distillation using a rotary evaporator under gradually increased temperature from 40 to 90°C and a retention time of between 10 and 20 minutes. Anaerobic digestion tests subsequent to different pretreatment variants were conducted at an organic loading rate of 0.25 g DM of fibers per 10 ml of inoculum. Different OLRs of between 0.16 and 1 g DM per 10 ml of inoculum were tested as well.
Almost all pretreatment variants revealed a substantially higher methane yield of between 17 and 80 % with an optimum at a treatment time of 3 days and a treatment temperature of 22°C. The methane formation rate was also highly increased. Tests with different OLRs revealed a particularly increased methane yield of 178 % for fibers separated from raw swine manure at an OLR of 0.16.

Yang et al. (2014) used **aqueous ammonia** for pretreatment of wheat straw prior to anaerobic digestion. The wheat straw was dried, chopped, and ground to a particle size between 5 and 10 mm prior to mixing it with water and ammonia in plastic bags. Aimed moisture contents of substrate were 30, 60, and 80 %, ammonia dosages of 2 %, 4 %, and 6 % on DM basis. The substrates were incubated at 35 ± 1°C, incubation time was determined by pH values. The treated and untreated wheat straw was tested in batch anaerobic digestion for methane yields with OLRs of 50, 65, and 80 $g \cdot l^{-1}$.
Higher methane yields due to soaking the wheat straw in aqueous ammonia were achieved in each case. A dose of 4 %, a moisture content of 8 %, and an OLR of 65 $g \cdot l^{-1}$ was presented as optimal conditions, leading to a methane yield increased by 36 %.

Song et al. (2013) investigated the effect of a pretreatment of rice straw with **hydrogen peroxide**. The rice straw was cut to 20 to 30 mm lengths with a grinder. 500 g rice straw were mixed with 1, 2.5, and 4 % of H_2O_2 in 1 liter beakers and water was added to that mixture until a solid to liquid ratio of 1:3 was reached. The beakers were then stored at ambient temperatures for 1, 4, and 7 days respectively before drying at 80°C for 48 hours. Methane yields were determined by batch anaerobic digestion tests.
Three (3) % H_2O_2 concentration, 6 days pretreatment time, and a substrate/inoculum ratio of 1:1 were presented as optimal treatment conditions. An 88 % higher methane yield than that obtained from untreated rice straw was achieved.

Mixed forms

The impact of **thermo-chemical pretreatment** using **sodium hydroxide** at **elevated temperatures** on the anaerobic biodegradability of pig manure was analyzed by Carrère et al. (2009). A mixture of sodium hydroxide and pig manure (adjusted to pH 10 or 12) was pretreated in a 2 liter glass reactor at temperatures below 100°C and in a 900 ml reactor Zipperclave (Autoclave France) at temperatures higher than 100°C. Treatment times were 3 hours for 25 and 90°C and 20 minutes at temperatures between 135 and 190°C. Batch anaerobic digestion tests were conducted for evaluating the methane potential. The pretreated manure was therefor mixed with the anaerobic sludge, oligo nutrients and buffer solutions.
The thermo-chemical pretreatment led to decreased methane yields for the pH 12 treatment in every case. At pH 10 the methane yield increased by 78 % for the variant pretreated at 190°C.

The effect of pretreating rice and triticale straw for subsequent biomethanation using **N-methylmorpholine-N-oxide (NMMO) and elevated temperature** was monitored by Teghammar et al. (2012). Before pretreatment the samples were cut to sizes of less than 10 mm. Pretreatment was conducted using a commercial grade NMMO solution concentrated to 85 % and supplemented by 0.25 g/l propyl galate. This solution was mixed with straw or spruce to a ratio of 7.5 % or 6 %, respectively, before it was kept at 130°C between 1 and 15 hours. The pretreated material was filtered and washed with boiling water to completely remove the NMMO, then freeze-dried and stored at 4°C before batch anaerobic digestion tests were performed at thermophilic conditions (55°C).
The effect of a combination of chemical and thermal pretreatments led to a 7 times higher methane yield (in this case related to carbohydrates) at treatment periods of 1 hour and 3 hours for rice straw and of 15 hours for triticale straw after six weeks of anaerobic digestion. An accelerated methane formation was not observed.

The utilization of concentrated **NMMO and temperatures** of between 90 and 120° as pretreatment option for oil palm empty fruit bunches was also investigated by Purwandari et al. (2013). The raw material was shredded, ground, and sieved in order to achieve particle sizes of 0.42 mm. Six (6) gram of raw material was soaked in 94 g of a mixture of NMMO solution (concentrated to between 73 and 85 %) and 0.6 $g \cdot l^{-1}$ propyl gallate for 1 to 5 hours at temperatures between 90 and 120°C. The process was terminated by adding 150 ml boiled deionized water, solids were separated by vacuum filtration and washed with hot water until the filtrate was clear. Batch anaerobic digestion tests were performed at thermophilic conditions (55°C) for 50 days.

The methane yield of oil palm empty fruit bunches was increased by 48 % in maximum compared to untreated material. Treatment conditions for achieving this result were 120°C, NMMO concentrated to 85 %, and 3 hours of treatment time.

Kabir et al. (2014) treated barley straw with a **NMMO solution** concentrated to 85 % at a **temperature** of 90°C for 3 to 30 hours. Afterwards, dissolved materials were recovered using distilled water, vacuum filtrated and washed with hot distilled water until a clear filtrate was achieved. Subsequent batch anaerobic digestion tests were performed at thermophilic temperature (55°C).
An increase in methane yield was observed in every case, with the highest (+92 %) at a treatment time of 7 hours.

Michalska et al. (2012) tested the effect of a pretreatment of *Miscanthus giganteus*, *Sida hermaphrodita* and *Sorghum bicolor* (L.) Moench by **Fenton's reagent and enzymes**. The biomass was dried and ground to obtain particles of 0.1 to 1 mm. The milled material was extracted with 96 % ethanol and rinsed with distilled water until the pH of the rinsate was neutral. Afterwards, the material was dried at 45°C. Five (5) g biomass was suspended in 100 ml of distilled water and the pH of the mixture was adjusted to 3 using diluted sulfuric acid. Between 1 and 15 $g \cdot l^{-1}$ of Fe^{2+} and 5 to 40 $g \cdot l^{-1}$ of 30 % H_2O_2 were added to the suspension to perform Fenton's oxidation. In variants with precipitation of iron (III) hydroxide the pH was raised to 11 using 20 % NaOH, the sample was placed in a water bath at 50°C for 30 minutes, centrifuged at 6,939 g for 5 minutes, the pellet obtained was rinsed by vacuum filtration with distilled water until the pH of the filtrate was neutral, and finally the material was dried at 45°C. For enzymatic hydrolysis 5 g of the respective material were suspended in 100 ml of 50 mmol citrate buffer solution,160 $EGU \cdot g^{-1}$ DM of cellulase and 17.2 $CBU \cdot g^{-1}$ DM of cellobiase were added, and the sample was kept for 24 hours at 50°C. The mixture of pretreated material and inoculum was adjusted to pH 7 using $NaHCO_3$ before batch anaerobic digestion tests at mesophilic conditions (37°C).
A relative comparison is not possible as the authors stated no biogas production from raw materials. Results presented are 13.6 l_N biogas per kg DM for *Miscanthus*, 25.2 $l_N \cdot kg^{-1}$ DM for *Sorghum,* and 26.1 $l_N \cdot kg^{-1}$ DM for *Sida*.

Bruni et al. (2010) investigated the effect of a combination of **steam pretreatment and addition of H_2SO_4** on biofibers. The biofibers were gained from digestate from a biogas plant using a mixture of cow and pig manure, maize silage, and industrial by-products as feedstock. Mixtures of biofibers and 2.1 to 7 % w/w H_2SO_4 of between 7.4 and 14.5 % DM were prepared and steam-treated in a 3 liter vessel at temperatures between 155 and 180°C for 15 minutes without a fast pressure release after these 15 minutes that would have led to

steam explosion. Methane potential was measured in batch anaerobic digestion tests at thermophilic conditions.
Best results were obtained at 155°C, 12.4 % DM and addition of 2.1 % w/w H_2SO_4 (67 % increase of methane yield, FM related) and at 160°C, 11.1 % DM and addition of 2.3 % w/w H_2SO_4 (43 % methane yield increase, FM related).

Zhang et al. (2011) investigated the impact of **thermo-chemical** treatment on sun-dried cassava residues. Six (6) gram of cassava residues were mixed with sulfuric acid (concentration 1.32 to 4.68 %) in a solid-liquid ratio of 1:10 w/v. This mixture was then thermobarically treated at temperatures between 143.18 and 176.82°C for 3.18 to 36.82 minutes. Before batch anaerobic digestion tests at thermophilic conditions (55°C) the pretreated material was adjusted to pH 7.2 using $NaHCO_3$.
Pretreating cassava residues at 157.84°C for 20.15 minutes with addition of 2.99 % w/w H_2SO_4 led to an increase of 56.96 % in methane yield.

Fernandes et al. (2009) investigated the effect of **thermobarical and chemical treatment** on hay, straw, and bracken as pretreatment for subsequent anaerobic digestion. Raw materials were ground to particles of approximately 1 cm, homogenized to particles of less than 1 mm, and freeze-dried before the actual pretreatment with calcium hydroxide (10 %), ammonium carbonate (4 $g \cdot l^{-1}$), and maleic acid (5.8 $g \cdot l^{-1}$) and temperatures between 85 and 150°C for 0.5 to 16 hours. Batch anaerobic digestion tests were performed at mesophilic temperatures of 35°C with pH-neutralization and addition of phosphate buffer and trace elements and macro nutrients.
The methane yield was not increased by pretreating hay but decreased by 28 % in maximum (maleic acid treatment) whereas an increase in methane yield was observed for straw pretreated with ammonium at 120°C for 2 hours (+28 %) and for bracken pretreated with calcium hydroxide at 85°C for 16 hours (+143 %).

Dewatered pig manure was treated **thermobarically and chemically** by Rafique et al. (2010). 25 g of pig manure was mixed with 5 % $Ca(OH)_2$ and left for 1 hour to react before thermal treatment at temperatures between 50 and 150°C for 1 hour. After this treatment the manure was neutralized by adding HCl before methane yields were determined in batch anaerobic digestion tests for 29 days.
An increase of methane yield of 72 % was observed when dewatered pig manure was pretreated at 70°C for 1 hour.

Wet explosion in combination with H_2O_2 as oxidizing agent was applied to wheat straw as pretreatment for anaerobic digestion by Wang et al. (2009). Prior to wet explosion in a 2.8 l reactor at 150 to 195°C and 5 to 14 bar and a dose of 3 to 8 g H_2O_2 per 100 g DM of straw

the straw was chopped in a hammer mill to a particle size between 3 and 5 cm. The DM content of wheat straw treated was between 10 and 20 %. Methane potential was determined in thermophilic batch anaerobic digestion tests at 55°C.
Results presented show a decrease in methane yield between 11 and 6.5 % at pretreatment conditions of 6 g H_2O_2 and 180°C and DM contents of 10 and 15 %, respectively, compared to untreated material.

1.3.4. Short review on full-scale pretreatment

Mönch-Tegeder et al. (2014) used a **cross-flow grinder** (Bio-QZ, MeWa, Gechingen, Germany) for pretreating horse manure mainly consisting of straw used as bedding material. Two parallel digesters of equal volume were used for experiment: One fed with untreated horse manure, the other with mechanically pretreated horse manure, both replacing energy crops. Beside the (pretreated) horse manure, the feedstock was composed of solid and liquid manure from cattle and pigs, maize silage, grass silage, grain silage, and crushed grain. The experiments lasted 160 days, that is 2 hydraulic retention times of the digester.
A significant decrease in methane yields of both digesters during the first 80 days was observed. During the second 80 days the methane yields increased again. The mean value of methane yields of the second 80 days was 29.6 % higher for the digester using pretreated horse manure than for the digester using untreated material. The electric energy demand for the pretreatment was given with 11.3 $kWh_{el} \cdot t^{-1}$ FM.

In a techno-economical study using Aspen plus and Aspen Process Economic Analyzer Shafiei et al. (2013) evaluated the combination of a **steam explosion** and a full-scale biogas plant using wheat straw as feedstock. The plant is situated in Sweden; capacity was set to 200,000 t DM per year. Fifteen (15) digesters each of a volume of 3,150 m³, that is in sum 47,250 m³, were implemented into the model. The pretreatment method is based on a process design study of a steam explosion developed by Aden et al. (2009).
The methane production costs were calculated to 0.48 $€ \cdot m^{-3}$ CH_4 for wheat straw. The share of the pretreatment unit on total investment was calculated to 13 % but owing to pretreatment the methane production costs were reduced by 35.7 %. The energetic efficiency of the entire plant is given with 80 % comparing the energy input with the output, lignin, low pressure steam, and methane.

The energetic and economic feasibility of pretreating cow manure from slaughterhouse by **steam explosion** was investigated by Cano et al. (2014). The input data of the effect of pretreatment were gained in lab-scale experiments as described above (section 1.3.3.). Two (2) different scenarios were presented: One used natural gas for heat production for the pretreatment unit, the other used exhaust heat from combined heat and power unit (CHP). In

a very rough calculation the investment for such a pretreatment facility was integrated into the results. Procedural costs like labor costs or energy costs as for ancillary components necessary for operating the steam explosion were disregarded in every case.
Results of scenario 2 are an energy output increased by 29 % leading to an income from selling electricity gained from surplus methane of 10.3 €·t^{-1} FM. The costs – including investment and depreciation within 10 years – for a facility for pretreating 30,000 t FM·a^{-1} were roughly calculated to 1 M€. If the lifetime of this facility is also estimated 10 years it leads to treatment costs of 3.33 €·t^{-1} FM from investment and depreciation. Nothing is said about the energy requirement per ton of feedstock, for this treatment variant or the costs related to this.

Elbeshbishy et al. (2011) conducted lab-scale experiments on the effect of **ultrasonic pretreatment** on hog manure as shown above (section 1.3.3.). In an energetic and economic analysis they calculated the expenditures for electric energy for ultrasonication related to the surplus methane due to pretreatment and compared it with the costs for natural gas. Investment for the pretreatment unit, gas processing etc. and all procedural costs were disregarded.
The energy input for optimum scenario is given with 139 kWh_{el}·t^{-1} DM, leading to costs of 9.7 $ per ton DM of hog manure. The surplus in methane is given with 50.4 m³ CH_4·t^{-1} DM at a price of 0.28 $·$m^{-3}$ (that is the price for natural gas) leading to an income of 14.1 €·t^{-1} DM of hog manure. Related to FM these values are conterminous with an energy input of 13.0 kWh_{el}·t^{-1} FM with costs of 0.90 $ per ton FM and an income of 1.31 $·$t^{-1}$ FM of this particular hog manure.

For determining the effect of the application of an **enzyme preparation** Schimpf et al. (2013) conducted full-scale experiments in a commercial biogas plant equipped with continuous digesters of 2,000 m³. Two identical digesters were used, both fed with the same substrate, one of them with, the other without supplementary addition of enzyme preparation in a ratio of 100 g enzyme preparation per ton dry matter substrate. The experiments were conducted over a period of one year.
The results presented were divided into 3 periods: The first period showed an increased electricity production of 2.6 % and the third period of 4.7 %. During the second period no effect could be measured.

Although the utilization of **chemicals pretreating** feedstock for anaerobic digestion is also known from practice size agricultural applications, results dealing with the effect of this form of pretreatment are not available yet in scientific publications.

1.3.5. Assessment of different pretreatment options

The transferability of lab-scale experiments presented (see section 1.3.3.) into practice is debatable. Almost all test designs include at least one treatment before the actual pretreatment and often a treatment subsequent to the actual pretreatment. These additional treatments are disregarded in the respective studies and all effects are assigned to the actual pretreatment. For example, the biomass samples used were often comminuted before pretreatment, thus increasing the vulnerable surface, or adjusted to provide optimal conditions to subsequent biomethanation by utilization of chemicals.

Thus, most of the experimental designs disregard the characteristics of agricultural biomasses or residues commonly used in full-scale biogas plants. High-viscosity or even solidity, high abrasivity, and high inhomogeneity (thick pieces and impurities like sand, stones, metallic pieces, etc.) characterize these biomasses. Therefore, all mechanical parts have to be resistant to severe wear and parts should be avoided that move in a defined clearance or gap like cylinder and piston in pumps or blade and counter-blade for comminution. A batch pretreatment process fed by e.g. a wheel loader or a simple dosing feeder can be advantageous compared to a continuous pretreatment process using e.g. pumps. Nevertheless, a continuous feeding of the digesters is preferred.

Especially in the case of chemical treatments, the lab-scale process does not represent the sole addition of the respective chemical agent but is often used in combination with other, e.g. pH-stabilizing, chemical agents or at elevated temperatures or pressures. In addition, the chemicals used were neutralized or removed/recovered to ensure suitable properties of the biomass for subsequent biomethanation.

Criteria for assessing different pretreatment methods concerning their impact on a subsequent biomethanation are expenditures in terms of energy and costs and the (bio)toxicity of additives and discharges. The energy needed for pretreatment has different weights as electric energy is regarded more valuable compared to thermal energy that can be used only partially in technical applications. (Bio)toxicity of the discharges is to be regarded as weak point of high impact as it bears not only hazardous risks but can also contaminate the entire digestate of biogas process which is an economically and ecologically valuable fertilizer.

All methods of pretreatment for biomethanation discussed above bear advantages as well as disadvantages. An overview and qualitative assessment is given in Table 1.

As it is part of an energy conversion facility, special attention is given to the (own) power consumption. Even though the energy carrier biogas or methane can be placed on the market directly, the final utilization of this energy carrier is almost exclusively for combined generation of electricity and heat. This conversion can be off-site or, more common, on-site

using a CHP. Discussing the utilization of agricultural biomasses and residues, on-site conversion is focused, as in contrast to electricity grids, gas grids are often not available in rural areas. Main source of income is therefore the selling of electric energy, whereas thermal energy, as by-product of electricity generation is not or only partially used. Hence, pretreatment options with low electricity consumption are preferable but thermal energy consumption is negligible if exhaust heat from CHP is used. Considering these criteria solely and disregarding the energy expenses for production of chemicals or enzymes or enzyme mixtures, chemical and biological methods display much better results than physical methods.

Considering running expenditures, that are costs for electricity consumption, additives, installations (in form of depreciation of the investment and interest rate) and maintenance, physical methods are preferable as costs for chemical agents or enzymes or enzyme mixtures exceed all other costs.

Apart from the costs, dealing with toxic, caustic, or explosive chemicals can be challenging to the plant operator and the application of these will lead to (bio)toxic discharges.

Thermobarical pretreatment is to be considered as a variant with moderate electric and high thermal power consumption, hence appropriate for biogas plants with attached CHP as often available in agricultural context. Low to moderate installation and maintenance costs and no hazardous risk but a strong effect on biomethanation are further advantages of this pretreatment option. As no pumps or comminution are needed it is highly appropriate for common agricultural biomasses and residues as described above.

The advantages of thermobarical treatment and its good applicability in agriculture make it preferable for further research.

Table 1: Summary and assessment of regarded pretreatment methods

pretreatment method		technical equipment	assessment: expenditures: electric power consumption	expenditures: therm. power consumption	expenditures: additives, costs	expenditures: installations, costs	expenditures: maintenance costs	hazardous risks: (bio)toxicity of additives	hazardous risks: (bio)toxicity of discharges	expected effect on biomethanation
chemical	acids / bases / oxidants	chemically resistant vessel	+	++	+++	++	+	+++	o to +++	+++
physical	purely mechanical	mill, chopper / shredder	++	o	o	+	++	o	o	++
	steam explosion	multiple thermally and pressure resistant vessels (autoclaves)	++	+++	o	+++	++	o	o	++
		sonotrodes	+++	o	o	+++	++	o	o	++
	thermo(-barical)	thermally (and pressure) resistant vessel (autoclave)	++	+++	o	++	+	o	o	+++
	mixed forms	extruder	+++	o	o	+++	+++	o	o	++
		low-/high-pressure homogenizer	+++	o	o	+++	+++	o	o	++
biological	fungi / fungal enzyme mixtures	reactor vessel	o	+	++	+	+	+	o	++
	isolated enzymes	reactor vessel	o	+	+++	+	+	+	o	++

o = no effect / no change
+ = low effect / low change ++ = moderate effect / moderate change +++ = strong effect / strong change

1.4. Thermobarical pretreatment

Previous studies comparing different methods such as mechanical, thermal, chemical and/or biochemical pretreatment have identified thermobarical pretreatment (also called liquid hot water or thermal pressure treatment) as a promising innovative approach (Budde et al., 2008; Carlsson et al., 2012; Hendriks & Zeeman, 2009). In principle, high temperatures and pressures (range 140…250°C and 4…40 bar) are used to hydrolyze high–molecular substances (i.e. lignin, cellulose, hemicellulose) and thus anticipate the biological step. Consequently, applying strong physical conditions might circumvent the hydrolysis bottleneck and reduce the digestion time needed (Carrére et al., 2009; Chandra et al., 2012a, 2012b; López González et al., 2014; Menardo et al., 2011; Mladenovska et al., 2006; Rafique et al., 2010; Qiao et al., 2011; Ziemiński et al., 2014). Advantages of thermobarical hydrolysis (TBH) compared with other pretreatment methods are a very low electric energy input, no additives and a low degree of maintenance. On the other hand, the physicochemical processes of lignocellulosic biomass pretreatment also generate inhibitory compounds and may thus reduce the performance of anaerobic digestion (Horn et al., 2011; Owen, 1979).

When transferring this technology into practice, the implementation should preferably take place in existing biogas plants (Menardo et al., 2011), mostly equipped with continuous stirred tank reactors as digester (Weiland, 2008). Therefore, a modular design has been projected to ensure wide-range applicability. However, pretreatment of various feedstocks challenge sustainable production in terms of greenhouse gas (GHG) mitigation, efficient energy conversion, or profitability (European Commission, 2010). The GHG emissions of biogas production are mainly determined by the type of feedstock and its origin (Fritsche, 2007; Seeberg-Elverfeldt, 2010). In general, a thermobarical process involves higher energy input and costs.

2. Objectives

The objective of this study is to determine and to assess the effects of thermobarical pretreatment of dairy cattle waste on anaerobic digestion. For this purpose a test device is to be designed and installed in the laboratory. The experiments are to be conducted with an emphasis on differences in cattle waste characteristics, temperature range and the associated saturated water vapor pressure, as well as duration of treatment. After pretreatment the material is to be investigated in batch anaerobic digestion tests in order to evaluate the overall impact on methane formation rate and yield.

A calculation based on the experimental data gained is to be applied to evaluate the technical, economic and environmental viability of pretreating cattle waste in the full-scale biogas process assuming that a combined heat and power unit is available as heat source for process energy. Energy and GHG emission balances are to be calculated and profitability investigated to estimate environmental and economic impacts of the designated thermobarical pretreatment of cattle waste. The assessment will not address the energy conversion route as such. The study will focus on the pretreatment of feedstock and the impact of the particular processual steps. Thus, the results presented will refer to the differences in pretreatment.

3. Materials and methods

3.1. Raw materials and mixtures

Different types of cattle waste were used for the laboratory experiments and calculations (Budde et al., 2014). They were obtained from two dairy cattle farms in the North-East of Germany, Fehrbellin (plant 1, abbreviated below to P1) and Groß-Kreutz (plant 2, abbreviated below to P2). Two kinds of raw materials were collected from each source: solid cattle manure (SCM) and liquid cattle manure (LCM). The latter includes parts of the litter and feed residues that fall through the slatted floor of high-performance dairy cattle housing in both places. SCM from P1 contained less straw than SCM from P2 as the latter was used for dry cows and heifers.

In addition to samples of single raw materials, mixtures were used to improve hydrolysis and pumpability. They were prepared separately for each source: solid cattle manure and water (P1-SCMW and P2-SCMW) and solid and liquid cattle manure (P1-SLCM). Chemical characteristics of the raw materials and mixing ratios are summarized in Table 2.

All raw materials were chemically analyzed directly after sampling and mixtures directly after preparation. Both raw materials and mixtures were stored in 40-l-barrels at 5°C until the experiments were conducted. They were covered with carbon dioxide dry ice granules to ensure anaerobic conditions and to prevent spoilage of the material.

Calculations of methane yields refer to a fresh matter base as the daily amount of feedstock to be pretreated is limited by the TBH device vessel-volume. The fresh matter volume flow to be pretreated is 12 $m^3 \cdot d^{-1}$ for any feedstock. Mass flows were calculated using (bulk) densities of 1,000 $kg \cdot m^{-3}$ for LCM and 800 $kg \cdot m^{-3}$ for SCM (Rühlmann, 2000). The density of SLCM was set to 1,000 $kg \cdot m^{-3}$, assuming that the spaces in the solid cattle manure are completely filled with liquid. The fresh matter mass fraction of SCM in SLCM is 0.327. The resulting mass flows of the different feedstocks are 0.1389 kg $FM \cdot s^{-1}$ in the case of LCM and SLCM and 0.1111 kg $FM \cdot s^{-1}$ in the case of SCM. The annual average temperature of fresh solid and liquid cattle manure is set to 15°C.

Table 2: Origin of raw materials, mixing ratios and chemical characteristics

origin	raw material (abbreviation)	mixing ratio	pH	DM	ODM	OM[a]	VOA	crude fiber	NDF	ADF	ADL	crude fat	sugar value[b]	total as acetic acid[c]	furfural	5-hydroxy-methyl-furfural	phenolic compounds
		(% w/w)		(% FM)			($g \cdot kg^{-1}$ FM)	(% DM)						($g \cdot l^{-1}$)	($mg \cdot l^{-1}$)		
plant 1	liquid cattle manure (P1-LCM)		6.9	7.8	6.4	7.2	8.0	24.4	47.2	39.1	14.8	5.0	4.9	-	-	-	-
	solid cattle manure (P1-SCM)		8.3	17.1	15.0	15.7	6.7	26.8	61.3	51.7	20.6	3.0	4.6	-	-	-	-
	solid cattle manure and de-ionized water (P1-SCMW)	40.1 59.9	7.7	6.9	6.0	6.3	2.7	23.0	46.9	36.9	12.7	3.1	0.3	2.0	0.0659	0.0511	1.0442
	solid cattle manure and liquid cattle manure (P1-SLCM)	27.8 72.2	6.9	8.8	7.4	8.1	7.3	28.3	52.8	43.3	14.8	3.6	5.0	6.7	0.0809	0.0485	0.8263
plant 2	liquid cattle manure (P2-LCM)		6.6	6.5	5.4	6.0	6.4	26.2	54.6	44.8	17.9	4.4	4.4	-	-	-	-
	solid cattle manure (P2-SCM)		8.5	19.9	16.3	16.9	5.9	27.4	55.0	50.5	21.6	3.2	4.7	3.0	-	-	-
	solid cattle manure and de-ionized water (P2-SCMW)	74.1 25.9	8.9	14.7	12.1	12.5	4.3	24.7	49.6	43.3	15.9	3.2	6.4	0.5	-	-	-

ADF – Acid detergent fiber; ADL – Acid detergent lignin; DM – Dry matter; FM – Fresh matter; NDF – Neutral detergent fiber; ODM – Organic dry matter; OM – Organic matter; VOA – Volatile organic acids

[a] OM = ODM + VOA

[b] sum of sucrose, fructose, and glucose

[c] sum of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and caproic acid

Maize silage is chosen as reference feedstock. It is the most frequent crop feedstock in anaerobic digestion in Germany today due to its high methane yield per hectare (DBFZ, 2010). Characteristics of maize silage are a bulk density of 300 $kg \cdot m^3$ (Köppen, 2002) and a fresh matter methane yield of 90 $l_N \cdot kg^{-1}$ FM (calculated according to data from KTBL (KTBL, 2010a)).

3.2. Lab-scale experiments

3.2.1. Test bench design for thermobarical pretreatment

A computer-controlled 600 ml Mini Reactor System, Model number 4568 (Parr Instruments, Moline, USA), was adapted to functional requirements for thermobarical hydrolysis of farm-based raw materials. The reactor specifications are as follows:

- Material: corrosion-resistant steel (T316)
- Pressure resistance of the installation: 200 bar
- Maximum operating pressure (limited by the blow-out disc): 40 bar
- Temperature resistance of the installation: 350°C
- Maximum operating temperature (limited by the temperature at a saturated water vapor pressure of 40 bar): 250°C
- Electrical mantle-heating: 780 W
- Stirrer power: 1/8 hp ≈ 93 W
- Stirrer torque: 6.75 Nm

In view of the high viscosity of the raw materials, the test bench is fitted with a strong magnetic coupling to transduce the rotational energy from the external motor to the inner-vessel stirrer. Furthermore, the reactor system is equipped with a ventilation valve to relieve pressure, an anchor mixer, a blow-out disc, thermocouples (Type J iron-constantan, Parr Instruments, Moline, USA) and a pressure transmitter (Type G2, Ashcroft, Stratford, USA). To record the vessel inner temperature, pressure and stirrer speed, an analog digital converter for data transmission was installed.

3.2.2. Thermobarical treatment

Temperatures for thermobarical treatment as well as the time for heating, the rotational speed of the stirrer and the number of replicates are summarized in Table 3.

Table 3: Variants and results of thermobarical treatment experiments (mean ± standard deviation of R replicates)

raw material	number of replicates R	set-point temperature	average of measured maximal temperatures	average time until set-point temperature is reached	average rotational speed		stirring device speed-change
					start	end	
		(°C)		(mm:ss)[a]	(rpm)		(%)
P1-LCM	4	140	143.5 ± 0.5	25:34	201	206	2.6 ± 1.5
P1-LCM	4	160	163.9 ± 0.9	27:48	210	219	4.7 ± 3.0
P1-LCM	4	180	180.9 ± 0.6	29:37	346	358	3.5 ± 1.1
P1-LCM	4	200	202.6 ± 0.7	36:50	360	375	4.2 ± 0.9
P1-LCM	4	220	222.0 ± 0.3	36:56	340	358	5.3 ± 1.8
P1-SCM	6	140	144.9 ± 0.8	15:37	323	340	5.4 ± 2.6
P1-SCM	6	160	162.8 ± 1.9	18:32	314	335	6.8 ± 2.2
P1-SCM	7	180	181.6 ± 1.4	27:55	322	347	8.0 ± 3.1
P1-SCM	6	200	200.6 ± 1.0	27:21	331	354	7.0 ± 2.6
P1-SCM	4	220	221.2 ± 0.8	31:11	331	384	16.2 ± 1.9
P1-SCMW	4	140	143.5 ± 0.9	23:40	353	362	2.5 ± 0.6
P1-SCMW	4	160	162.2 ± 0.7	25:52	337	351	4.2 ± 2.9
P1-SCMW	4	180	181.2 ± 0.3	31:47	329	346	5.3 ± 1.6
P1-SCMW	4	200	201.9 ± 0.3	35:44	302	323	6.8 ± 2.4
P1-SCMW	4	220	223.3 ± 1.6	40:24	311	330	6.3 ± 2.1
P1-SLCM	4	140	142.9 ± 1.4	25:21	191	199	4.2 ± 1.5
P1-SLCM	4	160	162.8 ± 1.0	24:43	196	206	5.4 ± 1.9
P1-SLCM	4	180	183.6 ± 1.3	30:05	202	218	7.6 ± 1.2
P1-SLCM	4	200	203.4 ± 0.5	34:45	358	383	7.1 ± 1.5
P1-SLCM	4	220	221.9 ± 0.7	42:56	351	381	8.6 ± 1.1
P2-LCM	5	140	142.0 ± 0.2	19:43	362	373	3.2 ± 0.9
P2-LCM	5	160	161.1 ± 0.6	26:46	368	382	3.8 ± 0.6
P2-LCM	5	180	180.9 ± 0.5	30:27	372	384	3.3 ± 0.6
P2-LCM	5	200	201.7 ± 0.1	35:14	381	397	4.4 ± 0.5
P2-LCM	5	220	222.0 ± 0.4	40:10	365	389	6.5 ± 1.9
P2-SCM	6	140	147.5 ± 1.5	13:53	357	376	5.2 ± 2.0
P2-SCM	6	160	161.4 ± 3.3	17:00	370	380	2.8 ± 1.3
P2-SCM	9	180	181.6 ± 1.1	23:34	376	397	5.7 ± 1.4
P2-SCM	9	200	200.7 ± 1.0	27:39	391	414	5.9 ± 0.9
P2-SCM	9	220	220.2 ± 0.9	32:10	390	420	7.7 ± 0.8
P2-SCMW	6	140	140.5 ± 0.6	22:15	338	355	5.0 ± 1.0
P2-SCMW	5	160	161.7 ± 1.1	20:38	351	376	7.4 ± 4.5
P2-SCMW	6	180	181.3 ± 0.9	24:10	351	370	5.4 ± 1.3
P2-SCMW	6	200	200.5 ± 0.5	28:48	364	388	6.7 ± 1.0
P2-SCMW	7	220	220.7 ± 0.7	30:36	390	423	8.8 ± 3.0

rpm – Revolutions per minute

[a] mm:ss – Time in minutes and seconds

The stirrer speed was adjusted manually, avoiding resonant frequencies. Treatment temperature was maintained for 5 minutes after reaching the designated value. The pressure values were equivalent to the temperature-specific saturated water vapor pressure. Before opening, the vessel was cooled until the inner-vessel temperature had almost reached ambient temperature and hence ambient pressure in order to prevent mechanical disruption of fibrous content by steam explosion.

By contrast with previous studies, the substrates were not mechanically prepared before thermobarical treatment in order to avoid any influence on hydrolysis and biomethanation due to increased surface areas.

Four (4) to 9 treatments were necessary (R = number of replicates) to obtain sufficient material for both the following chemical analyses and batch anaerobic digestion tests. The aliquots were put together to form one sample. An appropriate amount was used for chemical analysis. The remaining part was stored at -15°C until batch anaerobic digestion tests were conducted.

3.2.3. Batch anaerobic digestion tests

Biogas production and methane content of both untreated raw materials and TBH-treated feedstock were analyzed in batch anaerobic digestion tests. The methods used are described in detail in Herrmann et al. (2011).

Before starting, pretreated feedstock was defrosted at 5°C overnight. According to VDI 4630, tests were performed with 1.5 l inoculum in 2-l-bottles (VDI, 2006). The inoculum was derived from previous batch anaerobic digestion tests and is based on dairy cattle waste. The organic material (OM) used for batch anaerobic digestion tests is defined as the sum of volatile organic acids (VOA) and organic dry matter (ODM). Tests were conducted at $OM_{feedstock}$ to $OM_{inoculum}$ ratios of 0.5 to 0.7 (average chemical characteristic of inoculum: DM 3.23 %, ODM 1.95 %, VOA 1.75 $g \cdot kg^{-1}$). Biogas composition (methane, carbon dioxide, oxygen and hydrogen sulfide content) was measured during the batch digestion test using infrared absorption for CH_4 and CO_2 as well as electrochemical methods for H_2S and O_2 (GA 2000 Plus, Ansyco, Karlsruhe, Germany). All anaerobic digestion tests were performed in triplets. The inoculum without feedstock was run as a control in each case.

Methane formation period was calculated as the time until the average methane yield of pretreated feedstock reaches the average methane yield of raw materials after 30 days.

The significance of differences between methane yields from raw material and from treated feedstock as well as the comparison of these with the predicted methane yields was determined by multiple pairwise comparisons, applying the simulation method of Edwards & Berry (1987). Data were analyzed using SAS 9.1.3 (SAS Institute Inc., Cary, NC, USA), including the test procedures SIMULATE and CORR (Herrmann et al., 2011). The Pearson Product-Moment Correlation analysis is part of the CORR-procedure of SAS.

3.2.4. Analytical methods

Materials were analyzed according to standard laboratory methods as described by the Association of the Agricultural Investigation and Research Institutions (Suárez Quiñones et al., 2011; VDLUFA, 1997). Inhibitor content was determined by measuring the sugar by-products and lignin derived in supernatants using gas chromatography mass spectrometry (GC-MS). The GC-MS analysis was performed with an Agilent Technologies gas chromatograph 6890N Network GC System equipped with a mass detector Agilent Technologies 5973 Network Mass Selective Detector. A 25 m fused silica (cross-linked methyl siloxane) HP-5 was used as column with an internal diameter of 0.25 mm and a 0.25 micron film (Agilent Technologies UK Limited, Stockport, Cheshire), respectively. The flow rate of helium as the eluting gas was set to 1 $ml \cdot min^{-1}$. The GC oven conditions were programmed for an initial temperature of 45°C for 1 min and then raised at a rate of $10°C \cdot min^{-1}$ to 190°C ending at 190°C for 3 min. The GC-MS interface was kept at 280°C. The mass spectrometer scanned from 35 to 450 mass units. The electronic pressure control system was set to adjust the pressure according to the heat resistance of the column oven and the mass spectrometer was auto-tuned every day for maximum sensitivity. Parameters for analyses are summarized in Table 2 and Table 4. Inhibitors are presented as sum parameters of furfural, 5-hydroxymethyl-furfural and phenolic compounds.

Table 4: Chemical characteristics of pretreated feedstock after 5 minutes of treatment at set-point temperature

raw material	set-point temperature	pH	DM	ODM	OM[a]	VOA	crude fiber	NDF	ADF	ADL	crude fat	sugar value[b]	total as acetic acid[c]	furfural	5-hydroxy-methyl-furfural	phenolic compounds
	(°C)		(% FM)			($g \cdot kg^{-1}$ FM)	(% DM)						($g \cdot l^{-1}$)	($mg \cdot l^{-1}$)		
P1-LCM	140	7.4	8.1	6.7	7.5	8.1	24.0	51.5	32.4	9.6	-	0.3	11.1	0.0469	0.0000	0.3007
	160	7.6	7.7	6.4	7.2	8.0	26.2	49.8	35.2	11.4	4.2	0.3	9.6	0.0538	0.0151	0.6277
	180	7.3	6.9	5.6	6.5	8.6	22.6	37.4	31.5	10.6	5.2	0.4	8.8	0.0536	0.0051	0.7200
	200	7.1	6.7	5.5	6.3	8.1	30.8	38.1	35.3	11.5	5.5	0.3	9.7	0.0582	0.0482	1.0138
	220	6.2	6.1	4.9	5.7	7.2	30.4	34.2	35.4	12.0	6.2	0.2	6.3	0.2102	0.0259	0.5735
P1-SCM	140	8.4	15.3	12.9	13.5	6.1	29.5	61.6	47.5	16.4	2.9	5.4	3.0	-	-	-
	160	8.3	12.6	10.6	11.1	5.6	30.5	55.9	46.7	17.6	2.6	5.6	3.2	-	-	-
	180	7.7	15.2	12.7	14.0	13.2	32.0	53.6	46.6	17.7	2.8	5.7	8.9	-	-	-
	200	8.3	16.3	13.7	14.1	4.0	40.0	51.9	43.2	18.6	4.0	9.2	3.7	-	-	-
	220	7.2	14.1	11.9	12.5	6.0	39.7	44.0	48.5	21.6	2.5	10.2	3.5	-	-	-
P1-SCMW	140	7.8	6.8	5.5	5.6	1.1	27.9	54.3	41.6	13.3	3.9	0.3	4.5	0.0107	0.0000	0.7836
	160	7.9	9.6	7.9	8.5	5.7	32.0	56.8	44.9	12.6	3.0	0.3	6.2	0.0200	0.0166	1.0877
	180	7.2	5.6	4.5	5.0	5.1	32.0	48.8	38.1	11.6	3.3	0.4	5.9	0.1339	0.0193	1.5945
	200	6.0	6.0	5.1	5.6	5.2	35.7	49.4	40.6	12.0	1.9	0.3	5.9	0.2031	0.0371	1.7764
	220	4.9	3.3	2.6	3.0	4.0	30.0	43.7	34.0	9.5	2.2	0.3	4.2	0.0821	0.0067	1.8119
P1-SLCM	140	7.4	7.3	6.0	6.8	8.4	30.6	60.6	44.3	15.0	3.3	7.7	9.3	0.0435	0.0017	1.1550
	160	7.5	9.0	7.4	8.2	7.8	32.5	56.8	48.3	17.7	3.1	7.9	8.6	0.0146	0.0027	1.3009
	180	7.4	7.5	6.1	6.9	8.4	26.6	45.1	36.2	10.3	3.9	0.4	10.5	0.1755	0.0086	1.8281
	200	7.8	7.4	6.2	6.6	4.7	36.3	42.3	38.2	11.9	4.2	0.4	4.5	0.1506	0.0000	1.9388
	220	7.4	8.4	6.7	7.0	3.4	29.5	35.4	32.4	8.3	3.4	0.5	2.1	-	-	-

raw material	set-point temperature	pH	DM	ODM	OM[a]	VOA	crude fiber	NDF	ADF	ADL	crude fat	sugar value[b]	total as acetic acid[c]	furfural	5-hydroxy-methyl-furfural	phenolic compounds
	(°C)		(% FM)			($g \cdot kg^{-1}$ FM)	(% DM)						($g \cdot l^{-1}$)	($mg \cdot l^{-1}$)		
P2-LCM	140	6.8	7.1	5.9	6.6	6.8	26.4	55.3	42.3	19.5	4.8	4.5	7.3	0.0754	0.0262	0.3495
	160	6.5	7.1	5.9	6.6	7.0	27.6	53.6	40.3	16.4	3.8	5.3	7.4	0.0900	0.0212	0.3330
	180	6.2	7.5	6.3	7.0	7.7	33.6	52.6	42.3	25.9	3.8	5.8	8.3	0.0915	0.0379	0.6040
	200	5.4	6.4	5.2	6.0	8.0	32.4	39.6	34.9	16.6	3.4	7.1	8.9	0.3183	0.1038	0.7092
	220	5.0	6.7	5.4	6.4	9.1	32.7	39.0	36.1	16.5	4.2	4.2	9.5	0.3336	0.0660	0.9291
P2-SCM	140	8.4	19.9	16.4	16.9	4.3	29.0	56.5	50.1	21.5	2.9	8.2	3.8	0.0228	0.0118	0.3130
	160	8.6	21.1	17.5	17.9	3.4	31.5	56.5	51.3	20.2	2.7	7.0	2.6	-	-	-
	180	8.1	18.8	15.4	15.8	4.6	33.2	52.5	49.9	20.1	2.8	10.6	3.5	-	-	-
	200	7.3	18.7	15.1	15.7	5.9	34.0	43.0	3.0	0.9	3.4	8.7	3.6	-	-	-
	220	5.4	16.9	13.3	14.2	8.3	33.0	40.4	3.1	0.9	3.2	6.0	4.2	-	-	-
P2-SCMW	140	8.7	16.6	13.6	13.8	1.9	29.6	57.3	50.6	20.5	2.5	6.2	1.5	-	-	-
	160	8.6	16.0	13.3	13.6	2.7	33.0	55.3	51.6	19.8	2.4	6.5	1.8	-	-	-
	180	8.2	15.2	12.5	12.8	3.1	33.1	51.9	49.8	20.0	2.9	7.9	2.4	-	-	-
	200	7.5	14.3	11.6	12.0	4.2	32.4	41.7	46.2	29.4	3.0	9.1	2.9	-	-	-
	220	5.8	13.5	10.7	11.2	4.5	32.6	40.1	49.3	24.2	3.2	6.6	2.9	-	-	-

ADF – Acid detergent fiber; ADL – Acid detergent lignin; DM – Dry matter; FM – Fresh matter; LCM – Liquid cattle manure; NDF – Neutral detergent fiber; ODM – Organic dry matter; OM – Organic matter; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SCMW – Solid cattle manure and water; SLCM – Solid and liquid cattle manure; VOA – Volatile organic acids

[a] OM = ODM + VOA

[b] sum of sucrose, fructose, and glucose

[c] sum of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and caproic acid

3.3. Full-scale model and assessment

3.3.1. System boundaries, scenarios and functional unit

Full scale application of thermobarical pretreatment is assessed in terms of energy efficiency and greenhouse gas emissions following a life cycle assessment (LCA) approach (ISO 14044, 2006) as well as economic performance. In the following, boundaries necessary to perform this assessment are set up for the system before and after implementation of a TBH.

The system before the implementation of TBH is shown in Figure 2:

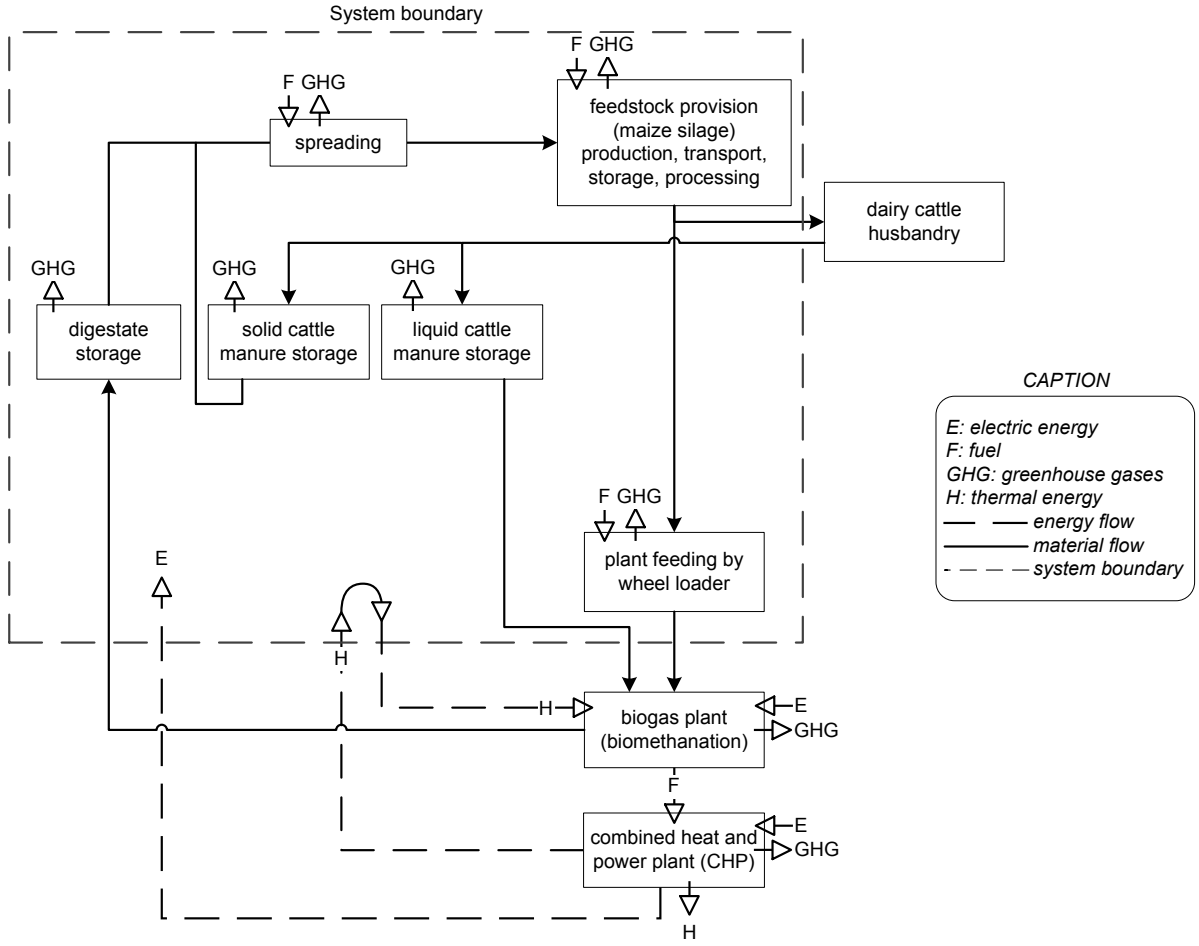

Figure 2: Flow scheme of mass, energy and fuel and GHG emissions of the reference system before implementation of a TBH device

In this case, maize silage is delivered to a plant site as biogas plant feedstock. The feeding to the biogas plant is accomplished by a wheel loader. Liquid cattle manure from stable is stored for an intermediate period (several hours up to several days) and then pumped to the biogas plant. Solid cattle manure from cattle breeding and digestate from biogas plant are stored for up to several months until they are spread on the field as fertilizer. The heat of combined heat and power generation from biogas is partly used for maintaining mesophilic conditions in the digester. Electricity, as the most valuable product, is sold.

Process alteration due to changes in feedstock and TBH treatment are regarded in scenarios considering:

- changes resulting from substitution of maize silage,
- changes in the feeding process (on-site process),
- parameters of decomposition of the different feedstock for GHG balance,
- changes in manure and digestate spreading procedure (off-site process).

The scenarios are named after the types of cattle waste and are further distinguished by the treatment temperature (T = 140, 160, 180°C) or lack of treatment respectively:

SCM: Pretreatment of solid cattle manure

LCM: Pretreatment of liquid cattle manure

SLCM: Pretreatment of a mixture of solid and liquid cattle manure

An overview of the different scenarios is shown in Table 5.

Table 5: Overview of the different scenarios in terms of raw material and pretreatment temperature

	pretreatment set-point temperature (°C)			
raw material	w/o	140	160	180
P1-LCM	X	X	X	X
P1-SCM		X	X	X
P1-SLCM		X	X	X
P2-LCM	X	X	X	X
P2-SCM		X	X	X

LCM – Liquid cattle manure; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SLCM – Solid and liquid cattle manure; w/o – without pretreatment

Figure 3 displays the alteration of the system by a retrofit of a TBH device. Energy equivalent shares of maize silage are substituted by a fixed volume of one of the three feedstocks. Thus, a unit volume of LCM, SCM or SLCM substitutes different gravimetric shares of maize silage.

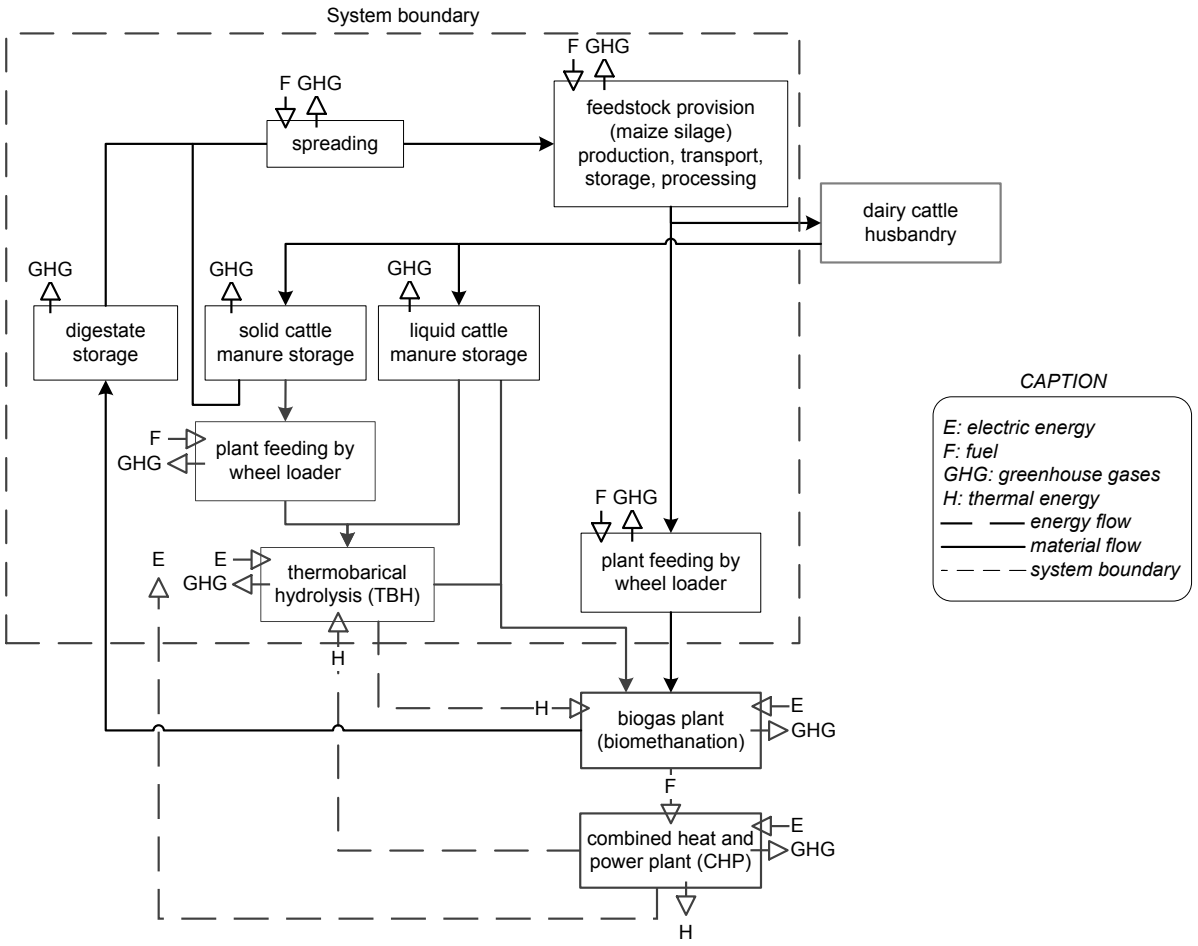

Figure 3: Flow scheme of mass, energy and fuel and GHG emissions of the modified system after implementation of a TBH device

LCM and SCM are pretreated by TBH and then fed to the biogas plant. LCM and SCM exceeding the daily load of the TBH device are not regarded in this analysis and remain in the usual process chain. The SCM is loaded by a wheel loader and LCM is pumped through pipes to the TBH vessel. Thermobarical pretreatment is driven by heat from CHP.

Scenarios SCM and LCM considered feedstock from two different biogas plant sites (P1 and P2) and therefore differing feedstock compositions (Budde, et al., 2014). Scenario SLCM was based on a mixture of solid and liquid cattle manure from biogas plant 1 only as feedstock. The utilization of untreated SCM was not regarded in the scenarios SCM and SLCM due to lesser digestibility and the risk of formation of floating layers.

Life cycle assessment of this study, based on methodology described in ISO 14044 (2006), focuses on energy efficiency and GHG emissions and comprises

- feedstock supply,
- transport of feedstock on an agricultural biogas plant site,
- storage of waste from dairy cattle farming (solid and liquid cattle manure) and of digestate from biogas process,
- thermobarical pretreatment of solid and liquid cattle waste and its mixture,
- their conversion to electricity and heat via biomethanation and combined heat and power plant,
- manure spreading with or without pretreatment and biomethanation.

All parameters were related to (theoretical) electricity output, the main product of the overall process with the functional unit 1 kWh_{el} as it allows the comparison with other bioenergy and non-renewable energy systems and pretreatment options related to them (Cherubini & Strømman, 2011).

The values related to time period are given as per year. An ‘integration’ over the year is necessary as the amount in terms of FM pretreated per year is a fixed value but the methanation capacity is influenced by the respective methane yield and by the OM content of feedstock.

Although the parameterization in per Mg implies that a size independent scaling would be possible – disregarding the fact that the amount of feedstock that can be treated in a given biogas plant is limited – values are also given as per Mg FM if related to mass, thus allowing to compare this study with other studies dealing with pretreatment options for biomethanation and giving mass related values only.

3.3.2. Principle construction and operational design of a full-scale thermobarical device and its retrofit to an existing biogas plant

The schematic flow chart of the thermobarical device and its integration into the biogas plant is shown in Figure 4. The TBH device is linked to the CHP via a thermal-oil circuit. Regarding feeding of the biogas plant, it is interposed in the pipeline of liquid cattle waste transport from stable to biogas plant. If liquid waste is unavailable, a recirculation pipeline from/to digester is to be retrofitted.

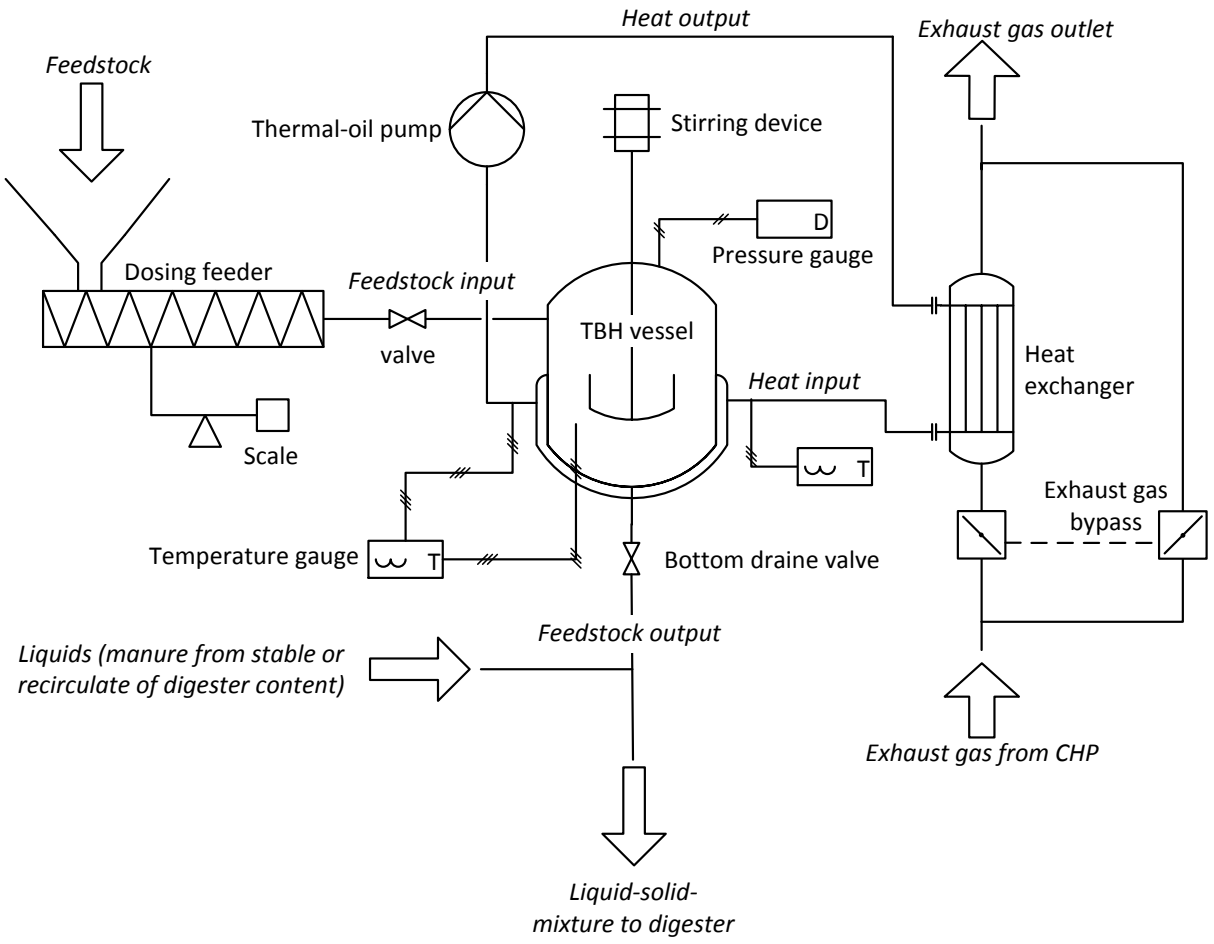

Figure 4: TBH facility. Schematic flow chart of the entire TBH facility (simplified) including the heat uncoupling from CHP and the feeding device (based on DIN EN ISO 10628, 2001)

The main components of this TBH device are a dosing feeder, a high temperature / high pressure vessel and a stirring device. The production of these components is assumed to be comparable to the rolling of stainless steel sheet. The thermal-oil facilities and the associated heat exchanger consisting mainly of stainless steel tubes are assumed to be comparable to cold drawn tubes. The masses of the respective components are summarized in Table 6.

Table 6: General input-data

General data		Reference
Density of methane at 0°C	0.72 $kg \cdot m^{-3}$	(VDI, 1991)
Lower heating value of methane	50.01 $MJ \cdot kg^{-1}$	(Beitz & Grote, 1997)
Molar mass of methane	16 $g \cdot mol^{-1}$	
Molar mass of carbon dioxide	44 $g \cdot mol^{-1}$	
Specific heat capacity of water	4.20 $kJ \cdot kg^{-1} \cdot K^{-1}$	(VDI, 1991)
Electricity costs	11.00 $ct \cdot kWh_{el}^{-1}$	Own assumption
Federal electricity-mix production costs	5.80 $ct \cdot kWh_{el}^{-1}$	(Stenull, M. & Raab, K., 2010)
Emissions from federal electricity-mix	0.611 kg CO_2-eq.$\cdot kWh_{el}^{-1}$	(Vogt, 2008)
Combined heat and power plant – nominal data		
Nominal electric power	330 kW	(GE Jenbacher GmbH & Co OHG, 2006)
Nominal thermal power	400 kW	
Electric efficiency	0.387	
Thermal efficiency	0.469	
Combined heat and power plant – exhaust gas		
Mass flow	1,878 $kg \cdot h^{-1}$	(GE Jenbacher GmbH & Co OHG, 2006)
Specific heat capacity	1.125 $kJ \cdot kg^{-1} \cdot K^{-1}$	
Input temperature	500 °C	unpublished engineering report
Output temperature	230 °C	
Thermal power	-158.46 kW	
Thermobarical hydrolysis device – components masses		
Dosing feeder	4,500 kg	unpublished engineering report
Vessel	3,500 kg	
Stirring device	1,000 kg	
Thermal-oil facility	4,000 kg	
Associated heat exchangers	1,000 kg	
Thermobarical hydrolysis device – energy for construction		
Stainless steel provision	24.3 $kWh \cdot kg^{-1}$	(ecoinvent, 2002)
Drawing of tubes	1.3 $kWh \cdot kg^{-1}$	
Rolling of sheets	3.1 $kWh \cdot kg^{-1}$	
Thermobarical hydrolysis device – emissions from construction		
Stainless steel provision	5.7123 kg CO_2-eq.$\cdot kg^{-1}$	(ecoinvent, 2002)
Drawing of tubes	0.39233 kg CO_2-eq.$\cdot kg^{-1}$	
Rolling of sheets	0.39272 kg CO_2-eq.$\cdot kg^{-1}$	

The entire facility is designed for a lifetime of 20 years.

Heat uncoupled from CHP exhaust gas is transported to the TBH device vessel via a thermal-oil circuit by a thermal-oil pump with a nominal electric power of 4.0 kW_{el}. The actual consumption of electricity depends on the running hours of the consumer loads. The amount of heat available depends on CHP power and the resulting temperature and mass flow of exhaust gas. To control the heat input into the feedstock, the vessel inlet and outlet temperatures of the thermal-oil are measured, as well as the temperature of the feedstock and the inner-vessel pressure. The heat-flow is controlled by using a bypass to the exhaust gas heat exchanger.

The solid feedstock is brought to a receiver tank of 12 m³ once a day where it can be mixed with liquid feedstock. A feedstock volume of 3 m^3 is delivered four times per day from the receiver tank to the vessel where the pretreatment takes place. Charging can be realized by a dosing feeder equipped with a scale for measuring the amount of feedstock. The pipe between dosing feeder and vessel is blocked by a valve during pretreatment. Different mixing elements are possible, but to avoid clogging it is recommended that a mixing stirrer agitating near the vessel inside wall be installed. Stirring power is approximately 1 $kW_{el} \cdot Mg^{-1}$ substrate at the beginning and decreases with increasing temperature and ongoing hydrolysis to 0.3 $kW_{el} \cdot Mg^{-1}$ substrate for temperatures above 100°C (expert interview).

The time for heating up feedstock to 100°C is estimated to be 1.61 h, and 3.22 h for reaching set-point hydrolysis temperature. This period of 4.83 hours is used for all designated set-point temperatures. The electric mixing power for SCM is calculated to be 1.0 kW_{el}. For further calculations it is assumed that the power for mixing LCM and SLCM equals that of SCM (unpublished engineering report).

After pretreatment the heated feedstock is released through a bottom drain valve using the water vapor pressure inside the vessel as driving force. Simultaneously, liquid feedstock is pumped through a pipeline that is linked to the outlet pipe. The mixtures of both treated feedstock and liquid feedstock are then delivered to the digester of the biogas plant.

3.3.3. Full-scale biogas plant

The modular concept of the TBH device designed allows a retrofit to almost all kinds of existing biogas plants. Therefore, the effect of thermobarical pretreatment is calculated without considering the particular biogas process in detail.

All calculations assume that the heat necessary to maintain mesophilic temperatures (T_{dig} = 40°C) is provided either directly from CHP to digester and/or via TBH.

Heat losses during pretreatment in comparison to losses in the heating system of the biogas plant digester are not regarded.

It is assumed that hydraulic retention time is not considerably decreased and viscosity not changed by the additional feedstock per day necessary to provide the same mass flow of methane (compared to maize silage).

Reduction in volume of feedstock due to biomethanation is not considered.

A possible change in feedstock degradation or degradability and stirring power is not regarded.

A wheel loader with a shovel-volume of 1 m³ is used for transport of solid feedstock to the feeding device of the biogas plant or the receiver tank of the TBH device. It is assumed that the distance between the storage location and the feeding device is 300 meters, that the distance is covered with an average speed of 20 $km \cdot h^{-1}$ and that both charging and discharging are done within 15 s. One charging process lasts 2.3 minutes under these assumptions.

LCM – also if used without pretreatment in biogas plant – does not require transport by wheel loader. But it could save an extra amount of maize silage if pretreatment enhances the fresh matter related methane yield. It could therefore save wheel loader trips that would otherwise have been necessary for transporting maize silage equivalent to the additional methane yield. SCM has a lower fresh matter related methane yield than maize silage but a higher bulk density. Hence, maize silage substitution changes the number of trips of the wheel loader necessary to provide the same amount of methane after biomethanation of SCM. In the case of the SLCM, the necessary extra trips and the saved trips corresponding to the respective mass fractions of LCM and SCM in SLCM are calculated. The calculation of methane yields of the respective feedstock at the respective pretreatment temperature is explained in detail in the next section (3.3.4.). The fresh matter volume-flow of feedstock and maize silage substituted and the numbers of additional or reduced wheel loader trips per day are calculated according to

$$\dot{V}_{FM,MS} = \dot{V}_{FS} \cdot \frac{Y_{CH4,FM,FS} \cdot \rho_{FS}}{Y_{CH4,FM,MS} \cdot \rho_{MS}} \quad (1)$$

The nomenclature for this and all following equations is presented in the list of symbols at the end of this thesis (supplement S1).

Heat is the main energy needed for TBH. It is provided by a combined heat and power plant. The CHP used for these calculations is a 330 kW_{el} biogas-otto-engine (Table 6).

The maximal set-point temperature $T_{set\text{-}point}$ for TBH process is 180°C. The temperature of uncoupled heat needs to be considerably higher in order to obtain a heat-flow that allows feedstock to be heated in a reasonable time. Therefore, the exhaust gas output temperature is set to 230°C. The thermal power available for the TBH process is calculated to be 158 $kJ \cdot s^{-1}$ from the characteristics of the exhaust gas of the CHP in the example. It is

assumed that CHP (and biogas plant) are in full operational state for 350 days (ADO - annual days of operation) or 8,400 hours (AHO - annual hours of operation) per year for all following calculations (FNR, 2010).

3.3.4. Energy balance

The energy balance considers the energy needed for construction materials E_{constr} as well as the electricity input (energy per time or per mass) for operation of the TBH device $P_{el,in}$ or $e_{el,in}$ and compares these inputs with the energy output, electric ($P_{el,out}$ or $e_{el,out}$) as well as thermal ($P_{th,out}$ or $e_{th,out}$), attained from pretreated feedstock via methane. Furthermore, the heat balance of heating up feedstock through TBH ($P_{th,FS}$ or $e_{th,FS}$) and heat transfer into digester ($P_{th,process}$ or $e_{th,process}$) is presented, as well as savings from energy needed for maize supply (δP_{MS} or δe_{MS}). The energy payback time or payback mass (EPBT or EPBM) is calculated in order to assess the energy efficiency.

The respective energy input for employment of agricultural machines for TBH device or biogas plant feeding and manure or digestate spreading was neglected. Calculation revealed values lying in most cases below 0.91 % of the entire energy input or output of the system, and never more than 2.45 %.

The energy for construction and provision of raw material E_{constr} in kWh has to be taken into consideration as part of an energy converting facility. The total energy demand for provision of stainless steel and for construction of a TBH device is calculated as 374,600 kWh.

The electricity demand $P_{el,in}$ or $e_{el,in}$ of the largest consumer loads of the TBH device, the stirrer and the thermal-oil pump, adds up to 42,000 $kWh_{el} \cdot a^{-1}$ or dependent on feedstock density either 10 or 12.5 $kWh_{el} \cdot Mg^{-1}$ FM.

In idealized calculation, thermal energy necessary to heat feedstock is affected by feedstock temperature T_{FS}, set-point temperature of the pretreatment $T_{set\text{-}point}$, and the density of the feedstock (the specific heat capacity of water and the volume flow of respective feedstock are assumed to be fixed values). The thermal input to feedstock $P_{th,FS}$ in $kWh \cdot a^{-1}$ for reaching set-point temperature during thermobarical hydrolysis is

$$P_{th,FS} = \dot{m}_{FS} \cdot c_{p,H2O} \cdot (T_{set-point} - T_{FS}) \cdot AHO \quad (2)$$

Related to fresh matter the thermal input $e_{th,FS}$ in $kWh \cdot Mg^{-1}$ FM is calculated according to

$$e_{th,FS} = c_{p,H2O} \cdot (T_{set-point} - T_{FS}) \quad (3)$$

After thermobarical hydrolysis, the heated feedstock is discharged into the biogas plant. It is assumed that there is no loss in thermal energy during transport of feedstock from the TBH device to the biogas plant. The heat input into the downstream biogas plant is determined by

the temperature difference between feedstock (T_{FS}) and digester content (T_{dig}) and the mass flow of the respective feedstock. The thermal energy input $P_{th,process}$, given in kWh·a^{-1} or $e_{th,process}$, given in kWh·Mg^{-1} FM, serves as process energy for the biogas plant: pretreatment and heating of feedstock contribute positive energy to the system while the untreated variants make a negative contribution. Process energy in kWh·a^{-1} is calculated

$$P_{th,process} = \dot{m}_{FS} \cdot c_{p,H2O} \cdot (T_{set-point} - T_{dig}) \cdot AHO \quad (4)$$

Related to fresh matter the process energy in kWh·Mg^{-1} FM is calculated according to

$$e_{th,process} = c_{p,H2O} \cdot (T_{set-point} - T_{dig}) \quad (5)$$

In the case of no treatment, the term $T_{set\text{-}point}$ is to be replaced by T_{FS}. The required heating of 'cold' untreated feedstock to mesophilic digester temperatures of 40°C leads to losses of 122,500 kWh_{th}·a^{-1} in the case of LCM and SLCM and 98,000 kWh_{th}·a^{-1} in the case of SCM. When related to fresh matter, it is 29.2 kWh_{th}·Mg^{-1} FM in any case.

It is assumed that the methane achievable from the respective feedstock in biogas plant equals the methane yield determined in lab-scale experiments.

The processing of LCM as well as the methane attainable from untreated LCM are assigned to the biogas plant as it is assumed that LCM is used or can be used in continuous stirred tank reactors without any pretreatment.

$$Y_{CH4,FM,LCM} = w_{OM,LCM} \cdot \left(Y_{30,LCM,T} - Y_{30,LCM,w/o}\right) \quad (6)$$

The methane available from SCM is completely allotted to the TBH as it is not suitable for utilization in conventional continuous stirred tank reactors without pretreatment.

$$Y_{CH4,FM,SCM} = w_{OM,SCM} \cdot Y_{30,SCM,T} \quad (7)$$

The shares of methane from LCM and SCM within SLCM have to be related to the respective feedstock. It is expected that the difference in methane yield of the respective feedstock – SCM or LCM – due to pretreatment corresponds with that in the mixture of both – SLCM. The ratio of methane from SCM to methane from LCM within SLCM at the different pretreatment temperatures T is then calculated according to

$$w_{CH4,FM,SCM,T} = w_{FM,SCM} \cdot \frac{Y_{30,SCM,T} \cdot w_{OM,SCM}}{Y_{30,LCM,T} \cdot w_{OM,LCM}} \cdot \left(w_{FM,SCM} \cdot \frac{Y_{30,SCM,T} \cdot w_{OM,SCM}}{Y_{30,LCM,T} \cdot w_{OM,LCM}} + \left(1 - w_{FM,SCM}\right)\right)^{-1} \quad (8)$$

The methane from LCM within SLCM $Y_{CH4,FM,(S)LCM,T}$ in l_N·kg^{-1} FM is

$$Y_{CH4,FM,(S)LCM} = \left[\left(1 - w_{CH4,FM,SCM,T}\right) \cdot Y_{30,SLCM,T} - \left(1 - w_{CH4,FM,SCM,w/o}\right) \cdot Y_{30,SLCM,w/o}\right] \cdot w_{OM,SLCM} \quad (9)$$

The methane attainable from SCM within SLCM is

$$Y_{CH4,FM,S(L)CM} = w_{CH4,FM,SCM,T} \cdot Y_{30,SLCM,T} \cdot w_{OM,SLCM} \quad (10)$$

Table 2, Table 7, and Table 8 show the values of untreated LCM and SCM allowing this calculation.

The methanation capacity P_{MC} in kWh·a^{-1} is calculated from the respective methane yields (Table 8)

$$P_{MC} = Y_{CH4,FM,FS} \cdot \rho_{CH4} \cdot LHV_{CH4} \cdot \dot{m}_{FS} \cdot AHO \quad (11)$$

Related to fresh matter the methanation capacity e_{MC} in kWh·Mg^{-1} FM is calculated according to

$$e_{MC} = Y_{CH4,FM,FS} \cdot \rho_{CH4} \cdot LHV_{CH4} \quad (12)$$

The methane is converted to electricity and heat by the CHP. The term $P_{el,out}$ or $e_{el,out}$ is the electricity in kWh$_{el}$·a^{-1} or kWh$_{el}$·Mg^{-1} FM achieved from the respective feedstock (Table 9).

The thermal output $P_{th,out}$ or $e_{th,out}$ in kWh$_{th}$·a^{-1} or kWh$_{th}$·Mg^{-1} FM is calculated by the thermal efficiency η_{th} of the CHP (Table 6).

The energy saved by substitution of maize silage (δP_{MS}), needed for the entire supply chain of maize silage, is in any case 0.162 kWh·kWh$_{el}^{-1}$ (Isermeyer et al., 2007). The values related (δe_{MS}) to fresh matter are displayed in Table 9.

The energy payback time or payback mass respectively is the time or FM mass needed for providing just as much net energy as is needed for construction of the power generation plant regarded. Assuming that only electric energy is used for production and processing of steel and semi-finished products, as is usual in modern steel plants, the energy payback time in (P[n]Y[n]M) adds up to

$$EPBT = \frac{E_{constr}}{P_{el,out} - P_{el,in}} \quad (13)$$

The energetic payback mass in Mg FM is calculated according to

$$EPBM = \frac{E_{constr}}{e_{el,out} - e_{el,in}} \quad (14)$$

3.3.5. Greenhouse gas balance

The net GHG balance GHG_{net} in kg CO_2-eq. per kWh_{el} or per Mg fresh mass (symbols indicated by a superscript double plus are related to fresh matter) results from emissions from TBH construction GHG_{constr} and operation $GHG_{el,in}$, saved emissions from SCM storage δGHG_{SCM}, and saved emissions from maize supply δGHG_{MS}:

$$GHG_{net} = GHG_{constr} + GHG_{el,in} + \delta GHG_{SCM} + \delta GHG_{MS} \quad (15)$$

Related to fresh matter the net emissions $GHG^{‡}_{net}$ are calculated according to

$$GHG^{‡}_{net} = GHG^{‡}_{constr} + GHG^{‡}_{el,in} + \delta GHG^{‡}_{SCM} + \delta GHG^{‡}_{MS} \quad (16)$$

The GHG payback time or payback mass (GPBT or GPBM) is the time or fresh matter needed for saving the same amount of GHG that accrued during construction of, in this case, the TBH device (GHG_{constr} or $GHG^{‡}_{constr}$).

It is assumed that the emissions which result from wheel loader employment for feedstock processing and from the entire process chain of spreading the agricultural manures can be neglected. Calculations revealed values below 0.88 % in most cases and never more than 2.27 %. Possible emission savings from avoiding LCM storage in open liquid manure storage facilities are assigned completely to the biogas plant and not considered here. It is further assumed that thermobarical pretreatment releases feedstock constituents which, without pretreatment, would not have contributed to methane emissions during storage of untreated LCM because of their lower degradability.

Emissions from TBH construction GHG_{constr} or $GHG^{‡}_{constr}$ are calculated based on parameters of semi-finished products, as explained for the energy input. The emissions sum up to 85,468 kg CO_2-eq., whereby the masses of raw materials and the emissions from provision as shown in Table 6 are taken into consideration.

One has to consider the emissions balance of grid electricity GHG_{grid} or $GHG^{‡}_{grid}$, as under German conditions, due to the difference in purchase prices of electricity and the granted feed-in tariff for electricity from biomass it is advantageous to use electric energy from the grid for the internal processes of a biogas plant (Table 6). Related to the electric energy produced the emissions $GHG_{el,in}$ in kg CO_2-eq. per kWh_{el} are calculated according to

$$GHG_{el,in} = \frac{P_{el,in} \cdot GHG_{grid}}{P_{el,out}} \quad (17)$$

Related to fresh matter the emissions $GHG^{‡}_{el,in}$ in kg CO_2-eq. per Mg FM are calculated according to

$$GHG_{el,in}^{\ddagger} = e_{el,in} \cdot GHG_{grid} \quad (18)$$

SCM is usually stored in heaps on a concrete surface. During storage the carbon within the SCM is aerobically reduced to CO_2 by microorganisms. It is expected that otherwise all carbon in CH_4 that is composed by microorganisms during anaerobic digestion would have led to CO_2 emissions. Therefore, the emissions due to utilization of SCM are calculated according to

$$\delta GHG_{SCM} = -\frac{M_{CO2}}{M_{CH4}} \cdot \frac{\dot{m}_{CH4,SCM}}{P_{el,out}} \quad (19)$$

Related to fresh matter these emissions are calculated according to

$$\delta GHG_{SCM}^{\ddagger} = -\frac{M_{CO2}}{M_{CH4}} \cdot Y_{CH4,FM,SCM} \cdot \rho_{CH4} \quad (20)$$

The emissions of CO_2-equivalents during rotting process are neglected.

In the case of SLCM only the emissions from SCM are taken into account.

The emissions from cultivation, harvest, transport and ensiling of maize silage from whole crop GHG_{MS} are set to 0.144 kg CO_2-eq.·kWh_{el}^{-1} (Isermeyer et al., 2007). It is further assumed that 25 % of the ensiled maize used is grown on former grassland. This land use change causes emissions of 0.0695 kg CO_2-eq.·kWh_{el}^{-1} (Isermeyer et al., 2007; Meyer-Aurich et al., 2012). Thus, the use of maize silage results in total emissions of 0.2135 kg CO_2-eq.·kWh_{el}^{-1}. The values related to fresh matter are displayed in Table 10.

The GPBT or GPBM respectively is the period or the fresh matter of the respective feedstock needed to save the same amount of emissions deriving from constructing the TBH device.

3.3.6. Profitability

The assessment of the economic performance of TBH is based on profitability, amortization period and CO_2 mitigation costs (CMC).

Costs arise from purchasing (C_{constr} or $C_{constr}^{\ddagger}$) and operating ($C_{el,in}$ or $C_{el,in}^{\ddagger}$ and C_{MT} or $C_{MT}^{\ddagger}$) the TBH device. Changes in wheel loader employment δC_{WL} or $\delta C_{WL}^{\ddagger}$ can save as well as cause costs, whereas changes in spreading-procedure $\delta C_{spreading}$ or $\delta C_{spreading}^{\ddagger}$ save costs in any case. Revenues in this analysis result from a bonus within the German feed-in tariff structure for electricity sales $\delta C_{el,out}$ or $\delta C_{el,out}^{\ddagger}$. The agricultural wastes used instead of maize silage are assumed to be available free of charge. All energy related cost factors related to TBH are balanced to a base of 10.06 ct·kWh_{el}^{-1}, derived from the costs of electricity production using maize silage δC_{MS} considering an average price of 35 € per ton of fresh

maize silage (Bönewitz, 2007). Related to fresh matter the costs in €·Mg^{-1} FM of electricity production using maize silage are calculated according to

$$\delta C_{MS}^{\ddagger} = \delta C_{MS} \cdot e_{el,out} \quad (21)$$

Hence, profit in ct·kWh$_{el}^{-1}$ or in €·Mg^{-1} FM is obtained as

$$Profit = C_{constr} + C_{el,in} + C_{MT} + \delta C_{WL} + \delta C_{spreading} + \delta C_{el,out} + \delta C_{MS} \quad (22)$$

$$Profit^{\ddagger} = C_{constr}^{\ddagger} + C_{el,in}^{\ddagger} + C_{MT}^{\ddagger} + \delta C_{WL}^{\ddagger} + \delta C_{spreading}^{\ddagger} + \delta C_{el,out}^{\ddagger} + \delta C_{MS}^{\ddagger} \quad (23)$$

Investment for TBH is estimated to 250,000 € (unpublished engineering report). Fixed costs of 17,500 €·a^{-1} comprise depreciation (life time 20 years, operation time 8,400 h·a^{-1}) and interest (at a rate of 4 %). Variable costs include electric energy consumption $C_{el,in}$ or $C_{el,in}^{\ddagger}$ (4,620 €·a^{-1}, own calculation), repair and maintenance C_{MT} or $C_{MT}^{\ddagger}$ (4,200 €·a^{-1}; KTBL, 2010b) and labor costs from wheel loader employment.

Changes in costs due to alteration in feedstock comprise costs of wheel loader and spreading. Investment of the wheel loader is 73,000 €. Fixed costs include depreciation (lifetime 10.3 years), interest (at a rate of 4 %), taxes and insurance (50 €·a^{-1}). Variable costs comprise diesel fuel (0.7 €·l^{-1}), lubricants (2 €·l^{-1}), repair and maintenance (1.41 €·h^{-1}). The costs of common labor are 13 €·h^{-1} (Hanff et al., 2010; KTBL, 2010b). These cost items are summed up to 36.73 cent per minute of wheel loader employment. Specific costs in cent per kWh$_{el}$ or in € per Mg FM are calculated depending on the volume of the respective feedstock to be transported for substitution of maize silage and the electric energy attainable or the FM mass flow of the respective feedstock.

The agricultural wastes would have led to costs for transport and spreading if not used for biomethanation. Costs that arise from transport and spreading of LCM or digestate sum up to $C_{spr,V}$ = 6.21 € per m^3. Costs $C_{spr,m}$ of 8.46 €·Mg^{-1} SCM result from transport and spreading of SCM (Hanff et al., 2010; Schindler, 2009; own calculation). Those costs are decreased by the saved spreading of digestate from feedstock to be substituted, in our case maize silage. The bulk densities of feedstock before biomethanation are ρ_{SCM} = 800 kg·m^{-3} in the case of SCM and ρ_{MS} = 300 kg·m^{-3} in the case of maize silage. After biomethanation the density of digestate ρ_{dig} is 1000 kg·m^{-3} in any case. The costs in ct·kWh$_{el}^{-1}$ arising from spreading digestate are

$$\delta C_{spr,dig,FS} = \frac{\dot{V}_{FM,FS} \cdot \frac{\rho_{FS}}{\rho_{dig}} \cdot C_{spr,V} \cdot ADO}{P_{el,out}} \quad (24)$$

Related to fresh matter the costs in €·Mg^{-1} FM arising from spreading digestate are calculated according to

$$\delta C^{\neq}_{spr,dig,FS} = \frac{\dot{V}_{FM,FS} \cdot \frac{\rho_{FS}}{\rho_{dig}} \cdot C_{spr,V}}{\dot{m}_{FS}} \quad (25)$$

As mentioned above, any processing of LCM is assigned to the biogas plant. As a result of increased methane yields through TBH, a concordant share of digestate from maize silage is replaced.

The saved spreading of SCM reduces costs, but the higher amount of digestate arising from SCM compared to digestate from maize silage causes additional costs for spreading. The costs in ct·kWh$_{el}$$^{-1}$ from spreading untreated SCM are calculated according to

$$\delta C_{spr,SCM,w/o} = \frac{\dot{V}_{FM,SCM} \cdot \rho_{SCM} \cdot C_{spr,m} \cdot ADO}{P_{el,out}} \quad (26)$$

Related to fresh matter the costs in €·Mg^{-1} FM from spreading untreated SCM

$$C^{\neq}_{spr,SCM,w/o} = C_{spr,m} \quad (27)$$

Costs in ct·kWh$_{el}$$^{-1}$ or in €·Mg^{-1} FM of spreading SLCM are compartmentalized according to its volumetric fractions.

The overall costs in ct·kWh$_{el}$$^{-1}$ for any feedstock sum up to

$$\delta C_{spreading} = -\delta C_{spr,SCM,w/o} + \delta C_{spr,dig,SCM} - \delta C_{spr,dig,MS} \quad (28)$$

Related to fresh matter the overall costs in €·Mg^{-1} FM for spreading are calculated according to

$$\delta C^{\neq}_{spreading} = -\delta C^{\neq}_{spr,SCM,w/o} + \delta C^{\neq}_{spr,dig,SCM} - \delta C^{\neq}_{spr,dig,MS} \quad (29)$$

Main income from biogas production is determined by feeding electricity into the grid with a given feed-in tariff. Despite a new Renewable Energy Sources Act that came into force in 2014, the following calculations are in accordance with the Renewable Energy Sources Act of 2012 (German Government, 2012a) as the TBH device – designed as modular concept – is aimed for retrofitting already existing biogas plants. The basic feed-in tariff for electricity generated from biomass amounts to 12.3 ct·kWh$_{el}$$^{-1}$. If only renewable resources such as energy crops etc. are used, an additional 6.0 ct·kWh$_{el}$$^{-1}$ can be obtained. Another 2.0 ct·kWh$_{el}$$^{-1}$ can be attained if animal waste or other agricultural residues are used. These 2 Cents are calculated with fixed methane yields for SCM of 53 l$_N$·kg^{-1} FM and for LCM of 17 l$_N$·kg^{-1} FM (German Government, 2012b). As the basic fee is allotted to the biogas plant, only

the additional fee for using agricultural wastes can be charged to the TBH, thus it is calculated by the shared contribution of feedstock constituents to generated electricity. The fee attainable is set at a fixed 2 cent per kWh_{el}. Related to fresh matter mass the fee attainable in €·Mg^{-1} FM is calculated according to

$$\delta C^{\neq}_{el,out} = 0.02€ \cdot kWh^{-1}_{el} \cdot e_{el,out} \quad (30)$$

The economic amortization period (ECAP) or amortization mass (ECAM) is the time in years and months (P[n]Y[n]M) or FM mass in Mg pretreated until investment for the entire TBH facility and all running expenditures – except for depreciation and interest rate – is paid back. In order to assess ECAP or ECAM, total investment is divided by profit. Depreciation and interest rate (in sum 17,500 €·a^{-1}) are added to profit as C_{TBH}, as part of profit already contains investment for such a TBH device in the form of depreciation and interest rate

$$ECAP = \frac{Investment}{Profit + Depreciation + Interest} \quad (31)$$

$$ECAM = ECAP \cdot \dot{m}_{FS} \cdot ADO \quad (32)$$

The CO_2 mitigation costs (CMC) in € per ton of CO_2-eq. (in addition to that of the downstream biogas plant) are deduced from the electricity production costs $C_{EP,TBH}$ (Profit without δC_{MS}) compared to the grid electricity-mix production costs $C_{EP,grid}$ (Table 6; Öko-Institut, 1998; Stenull & Raab, 2010).

$$CMC = \frac{C_{EP,TBH} - C_{EP,grid}}{GHG_{grid} - GHG_{net}} \quad (33)$$

3.3.7. Sensitivity Analysis

Sensitivity analyses were performed by alternating the following input parameters by ±50 %:

- stirring power exemplary both for changes in demand of electric energy of TBH and as parameter influenced by feedstock viscosity,
- investment for displaying changes in fixed costs,
- organic matter content of feedstock as example for changes in feedstock composition and for presenting the impact of changes of organic loading rate on the model output.

The output parameters chosen were:

- GHG as a parameter sensitive to changes in feedstock parameters and energy demand of the device but not influenced by changes of economical parameters,

- CMC as it is displaying the environmental impact *and* the costs occurring if using TBH in combination with an agricultural biogas plant as mitigation strategy,
- ECAP as it is sensitive to all input parameters that lead to changes in economic viability but disregards the environmental impact.

4. Results and discussion

4.1. Lab-scale experiments

4.1.1. Thermobarical pretreatment, chemical analysis, and batch anaerobic digestion tests

Chemical and physical characteristics of untreated feedstock are displayed in Table 2 (Budde et al., 2014). Dry matter contents of cattle slurry between 6 and 8 % are typical values for dairy cattle husbandry in Germany. Values for cattle dung typically range from 16 to 25 %. Thus, the feedstock used in these experiments represents average waste from dairy cattle. It is also common to use considerable amounts of straw as litter in stables which is reflected in the high crude fiber values of 23 to 28 %.

During treatment of feedstock, changes in viscosity could be observed from differences in rotational speed at the beginning and end of treatment. In all variants, an increase of up to 10 % in stirrer speed was observed between the beginning and end of the heat-up phase, including the 5-minute halt at the set-point temperature (Table 3). P1-SCM pretreated at 220°C revealed an even higher change of rotational speed of 16.2 %. The ongoing decrease in viscosity with rise in temperature is contrary to the results of Bougrier et al. (2008), without a change in viscosity for pretreatment temperatures above 150°C. Reasons for changing viscosity are the thixotropic characteristics of the manure (Plöchl et al., 2009) and the hydrolysis of corresponding fractions of the feedstock. The latter becomes obvious at the highest applied pretreatment temperature of 220°C. Only a small amount of fibrous components as well as some insoluble sediments remained in an almost watery, clear liquid. Tests with untreated liquid manure at ambient temperature showed that the thixotropic component produces a less than 3 % change in rotational speed.

Thermal treatment at higher temperature is known to promote the formation of furfural, 5-hydroxymethyl-furfural and phenolic compounds. These substances act as inhibitors for either hydrolysis or methane formation (Horn et al., 2011; Owen, 1979). In Table 4 values are presented for selected variants of thermobarical pretreatment. By comparison with Gossett et al. (1982), Owen (1979) and Barakat et al. (2012), the values determined in this study are several magnitudes lower. There is a general trend of increasing concentrations with increasing treatment temperature. The maximum increase of the sum of these substances is approximately threefold from 140 to 220°C.

Batch anaerobic digestion tests generally reveal higher methane yields for the treated variants (Table 7).

Table 7: Methane yields (mean ± standard deviation of three replicates), formation rates, inflection points and predicted methane yields (according to formula 34) of raw materials and different feedstock derived from batch anaerobic digestion tests

raw material	set-point temperature	methane yield	relative methane yield	formation period[a]	time at inflection point	methane yield at inflection point	average formation rate until inflection point	predicted methane yield
	(°C)	($l_N \cdot kg^{-1}$ OM)	(%)	(d)		($l_N \cdot kg^{-1}$ OM)	($l_N \cdot kg^{-1}$ OM·d^{-1})	($l_N \cdot kg^{-1}$ OM)
P1-LCM	untreated	203	100	30	7	111	16	203
	140[b]	306 ± 18	150	11	3	86	29	293
	160[b]	311 ± 2	153	17	3	108	36	344
	180	235 ± 13	115	10	7	158	23	250
	200	213 ± 8	105	17	5	96	19	227
	220	199 ± 3	98	>30	6	84	14	190
P1-SCM	untreated	168 ± 13	100	30	3	37	12	168
	140	186 ± 1	111	20	3	35	12	166
	160	187 ± 7	112	18	4	67	17	181
	180[b]	216 ± 8	129	10	2	60	30	221
	200[b]	202 ± 3	121	10	3	50	17	181
	220	158 ± 2	94	>30	3	34	11	165
P1-SCMW	untreated	203 ± 1	100	30	5	45	9	203
	140	215 ± 5	106	22	5	57	11	215
	160	197 ± 10	97	>30	2	48	24	278
	180	203 ± 12	100	28	5	64	13	222
	200	194 ± 9	96	>30	4	85	21	264
	220[b]	148 ± 6	73	>30	16	107	7	191
P1-SLCM	untreated	226	100	30	6	95	16	226
	140[b]	296 ± 4	131	15	3	94	31	319
	160	291 ± 2	129	14	3	99	33	329
	180	289 ± 12	128	11	3	96	32	323
	200	187 ± 24	83	>30	4	74	19	242
	220	166 ± 12	74	>30	4	54	14	212

raw material	set-point temperature	methane yield	relative methane yield	formation period[a]	time at inflection point	methane yield at inflection point	average formation rate until inflection point	predicted methane yield
	(°C)	($l_N \cdot kg^{-1}$ OM)	(%)	(d)		($l_N \cdot kg^{-1}$ OM)	($l_N \cdot kg^{-1}$ OM·d^{-1})	($l_N \cdot kg^{-1}$ OM)
P2-LCM	untreated	225 ± 7	100	30	5	75	15	225
	140	259 ± 3	115	17	5	113	23	263
	160	262 ± 7	116	13	5	115	23	265
	180	245 ± 11	109	12	5	126	25	276
	200	225 ± 32	100	30	3	69	23	265
	220	184 ± 13	82	>30	8	121	15	225
P2-SCM	untreated	162 ± 8	100	30	11	83	8	162
	140[b]	232 ± 16	143	13	5	62	12	215
	160[b]	255 ± 3	158	13	5	94	19	285
	180	177 ± 3	109	21	12	118	10	187
	200	180 ± 8	111	18	12	121	10	190
	220	135 ± 1	83	>30	16	107	7	152
P2-SCMW	untreated	182 ± 4	100	30	4	43	11	182
	140	206 ± 19	113	18	4	76	19	215
	160[b]	216 ± 7	118	14	4	85	21	224
	180[b]	219 ± 7	120	12	4	95	24	234
	200	197 ± 5	108	16	4	80	20	219
	220	152 ± 2	84	>30	6	76	13	190

LCM – Liquid cattle manure; OM – Organic matter; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SCMW – Solid cattle manure and water; SLCM – Solid and liquid cattle manure

[a] Time till the average methane yield of pretreated feedstock reaches the average methane yield of untreated feedstock after 30 days

[b] Significantly different to respective untreated raw material at $p < 0.05$, Adjustment = SIMULATE

The increase is strongly dependent on the feedstock used and the treatment temperature. Yield increase ranges from 5 % for P1-LCM to 58 % for P2-SCM. This is in accordance with other authors dealing with thermobarical treatment of animal manure, e.g. Mladenovska et al. (2006) found a 24 % increase in methane yield of the solid fraction of a mixture of cattle and swine manure at a temperature of 100°C and a treatment time of 20 minutes. A 49 % increase in methane yield was found by Carrère et al. (2009) pretreating pig manure at 150°C and up to 64 % at a temperature of 190°C. Dewatered pig manure was treated thermobarically by Rafique et al. (2010) leading to an increase of methane yield of 30 % if pretreated at 100°C for 1 hour. Menardo et al. (2011) treated raw solid swine manure at 120°C for 30 minutes resulting in a surplus in methane yield of 170 % in batch anaerobic digestion tests at mesophilic temperatures. Diluted cow and pig manure as feedstock was used by Qiao et al. (2011). In this study the thermal treatment led to a decrease in methane yield of 7 % in case of the cow manure but an increase of 15 % was observed for the pig manure.

In every case treatment at 180°C or lower shows the strongest positive effect on methane yield, while at 220°C the methane yields were always lowest. In most cases the highest methane yield coincides with the lowest time taken to reach the methane yield of untreated raw material after 30 days of batch anaerobic digestion. That could be achieved in 10 days as for P1-SCM, or in 22 days for P1-SCMW (Figure 5).

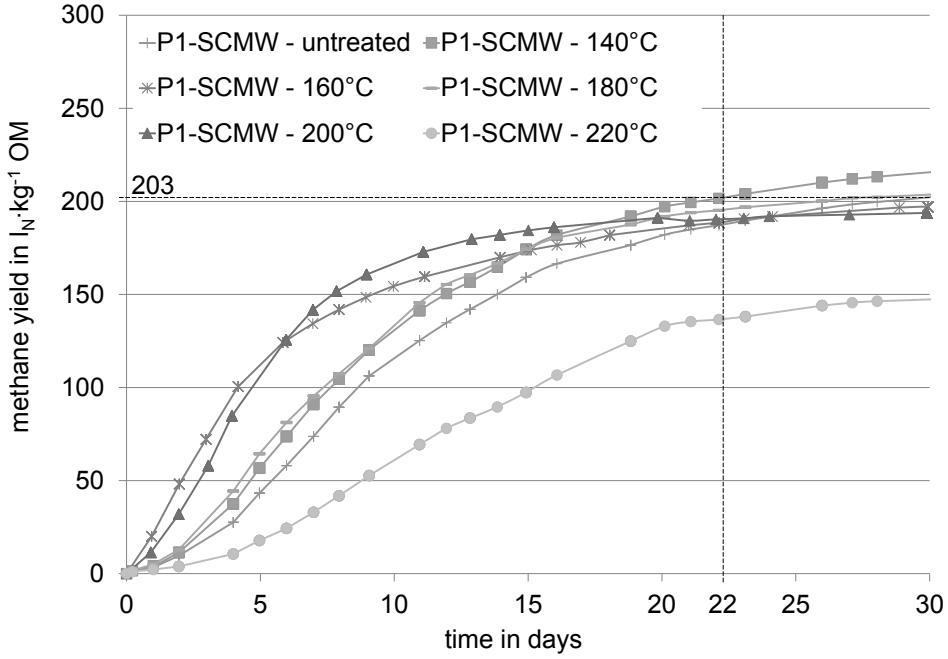

Figure 5: Cumulative methane yields from batch anaerobic digestion tests of untreated and treated solid cattle manure and water from origin P1. The vertical line indicates the time period in which the fastest variant reaches the methane yield of the untreated variant represented by the horizontal line. The results shown are generated from the mean values of three repetitions for treated variants. Untreated SCMW is a mean value of two repetitions

The methane yields of mixtures can deviate from the sum of the pure feedstock. P1-SCMW reveals the approximate organic matter related methane yield of pure SCM. However, SLCM (Figure 6) composed of 31 % organic matter from SCM and 69 % from LCM reaches a 10 % higher maximal methane yield, 296 $l_N \cdot kg^{-1}$ OM, than the sum of the respective constituents. The highest increase is observed at a temperature of 180°C: the yield of SLCM is 26 % higher compared with the respective yields of its constituents.

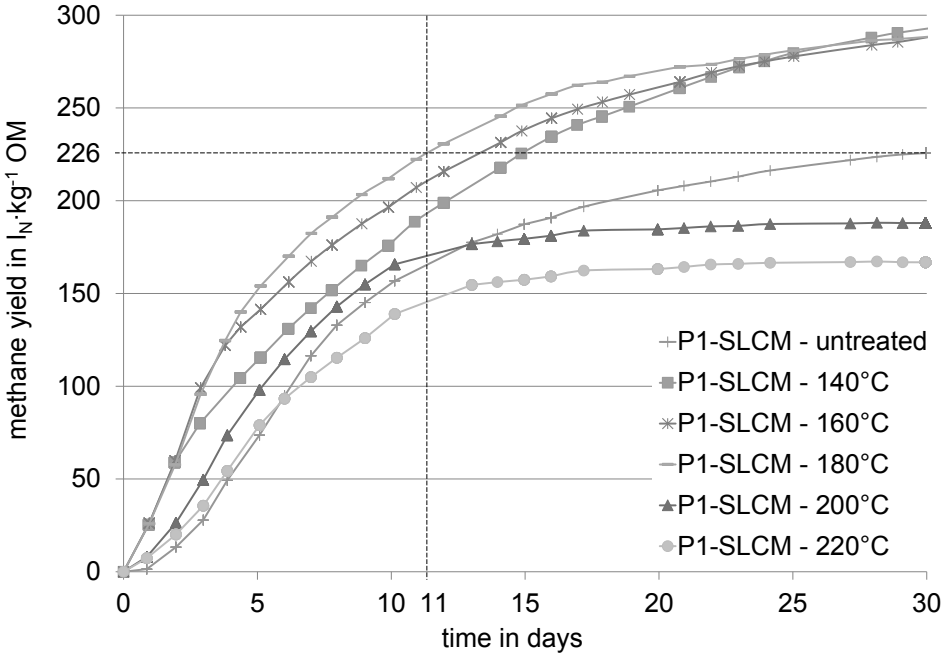

Figure 6: Cumulative methane yields from batch anaerobic digestion tests of untreated and treated solid and liquid cattle manure from origin P1. The vertical line indicates the time period in which the fastest variant reaches the methane yield of the untreated variant represented by the horizontal line. The results shown are generated from the mean values of three repetitions for treated variants. Untreated SLCM was not tested in repetition

4.1.2. Extended analysis of thermobarically caused hydrolysis and its impact on methane yields

There is an obvious correlation between the methane yields after 30 days and the average slopes of the yield curves until and the yields at the particular inflection points of treated and untreated feedstock (Table 7; Figure 7). This correlation is expressed by:

$$Y_{30,T} = Y_{30,w/o} + Y_{IP,w/o} \cdot \left(\frac{k_{IP,T}}{k_{IP,w/o}} - 1 \right) \quad (34)$$

in which $Y_{30,T}$ is the predicted methane yield (l_N CH_4·kg^{-1} OM) of treated feedstock after 30 days, $Y_{30,w/o}$ the methane yields of untreated feedstock after 30 days, $Y_{IP,w/o}$ the methane yields of untreated feedstock at inflection point, $k_{IP,T}$ the average formation rate (l_N CH_4·kg^{-1} OM·d^{-1}) of treated and $k_{IP,w/o}$ of untreated feedstock until inflection point. The term $k_{IP,T}$/ $k_{IP,w/o}$ is named K-value in the following.

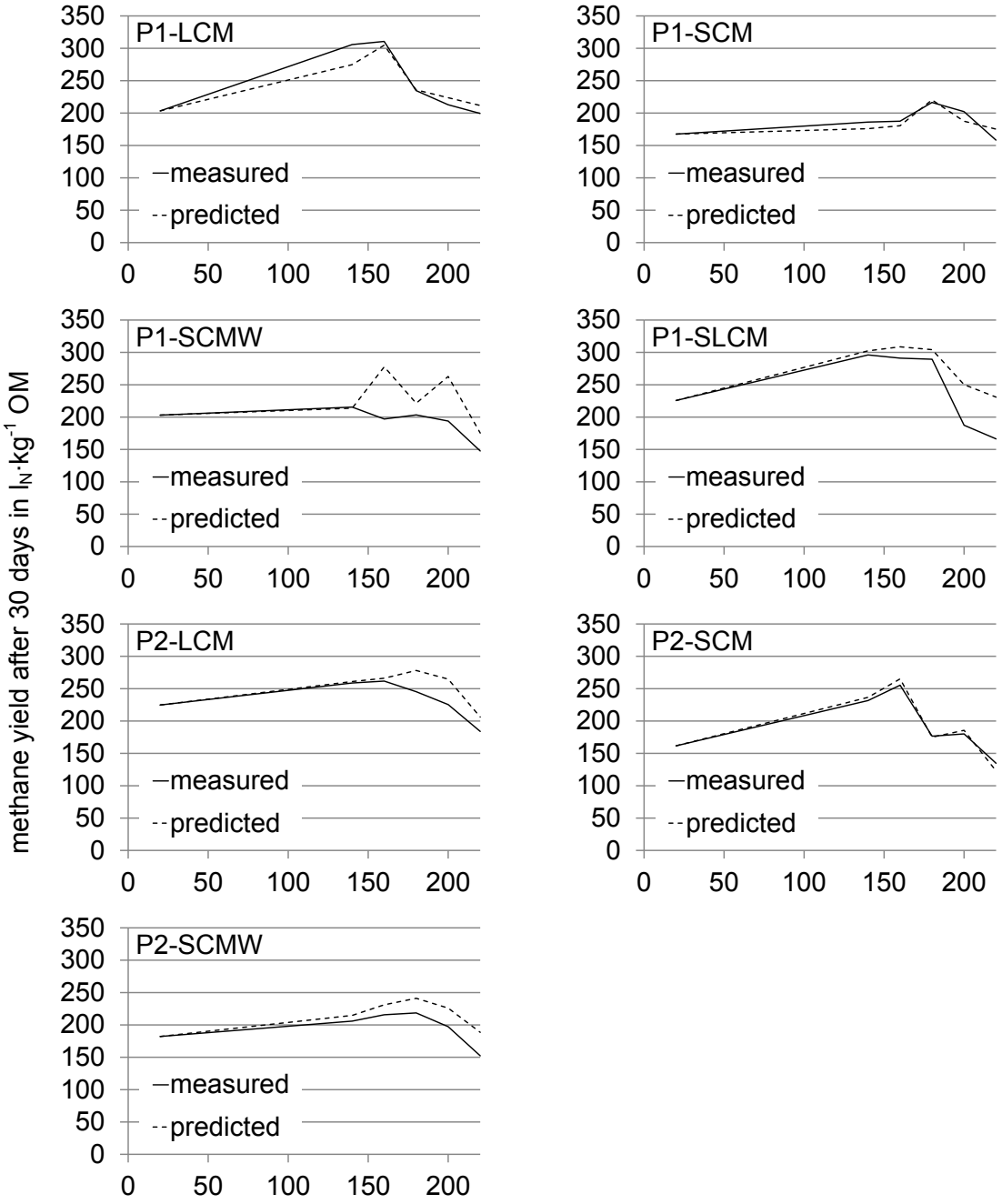

Figure 7: Measured methane yields after 30 days from batch anaerobic digestion tests and methane yields predicted (calculated according to formula 34) of untreated and treated feedstock. Untreated variants are displayed at 20°C (ambient temperature)

The above correlation is highly significant for the experiments conducted here with a Pearson correlation coefficient of 85.3 % (see section 3.2.3.). Therefore, it can be deduced that the alteration in yield is mainly influenced by processes taking place during this acceleration phase or the abundance of non-digestible constituents. It is assumed that thermobarical pretreatment also leads to free carbon inert to anaerobic digestion. At a temperature above

180°C a partial hydrothermal carbonization is likely, as reviewed by Libra et al. (2011) from numerous references.

The formation rate during the acceleration phase is usually determined by biological hydrolysis (Vavilin et al., 1996). The significant coincidence between the predicted and the measured surplus yield demonstrates that thermobarical hydrolysis not only improves the availability of less degradable constituents of feedstock but also exposes substances to methanogenic bacteria that would not be available if feedstock were hydrolyzed by hydrolytic bacteria only. Scanning electron microscope investigation reveals clear destruction of straw surfaces after thermobarical treatment (Figure 8).

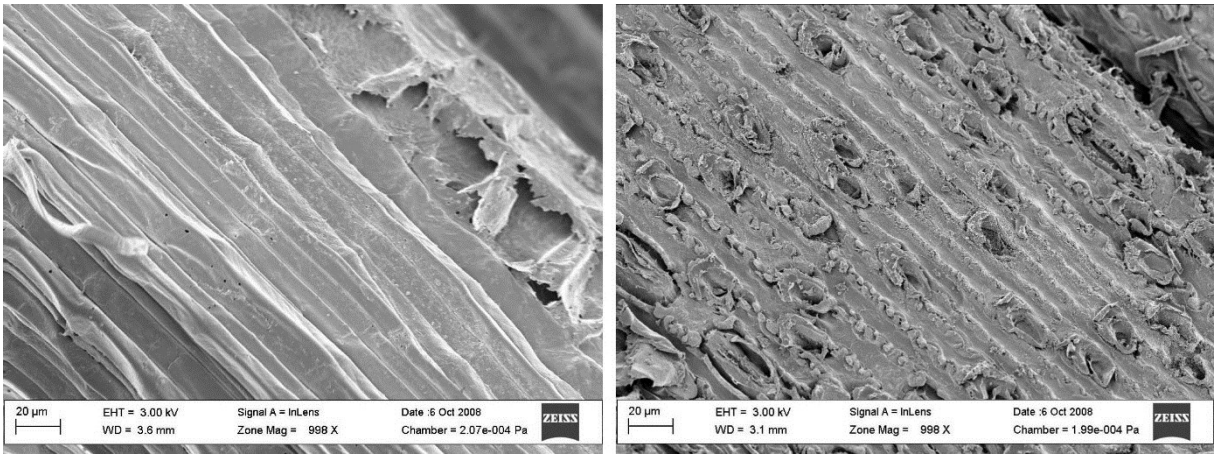

Figure 8: Untreated (left) and thermobarically treated straw (right) from solid cattle manure. The pictures show the surfaces of the straw particles examined, consisting of hemicellulose and lignin and other binding materials

In general, results show low methane yields for feedstock pretreated at higher temperatures as well as an obvious deviance between predicted and measured values. Possible reasons may be free carbon, as well as inhibitors formed during TBH treatment. It is assumed that mostly holocellulose is hydrolyzed through temperature and pressure. At higher temperatures lignin seems to be decomposed as well, as proved by the abundance of phenolic compounds. The sum of inhibitors (Table 2 and Table 4) and the difference between predicted and measured methane yields after 30 days (Table 7) have a significant correlation of 0.6638 for all feedstock variants except SCMs and P2-SCMW, for which it was physically impossible to determine inhibitors. Thus, the positive effects of improved hydrolysis on methane yields are counteracted by the inhibiting effect of furfural, 5-hydroxymethyl-furfural and phenol to a degree of 66 %. The remaining 34 % may be due to the free carbon, inert to anaerobic digestion, formed at higher treatment temperatures, or to continuing inhibition after the acceleration phase.

In the case of SCMs, there is a strong correlation between measured and predicted methane yields after 30 days. Therefore, it is assumed that free carbon is responsible for the decrease in methane yields for variants pretreated at higher temperatures. An increase in free carbon at higher treatment temperatures is likely, as burned material at the inner vessel wall could be detected by visual inspection. The development of burned material may be due to the low water content of SCM, the poor heat transfer into the material and therefore hotter inner walls of the vessel.

P1-SCMW reveals deviating behavior of methane yields as a function of treatment temperature (Figure 7). The yield at 160°C is clearly lower than at 140°C, as well as lower than that from untreated and treated material at 180°C. This behavior is also reflected in the deviation between measured and predicted values. It is not yet possible to explain these aberrations with the parameters determined.

In order to determine the optimal temperature for thermobarical hydrolysis, the K-value is plotted against treatment temperature. A log-normal function is used for the regression of these values:

$$K(T) = K_0 + a \cdot e^{-0.5 \cdot \left(\frac{ln(T/b)}{c}\right)^2} \quad (35)$$

in which K_0 (= 1) is the ratio of the average formation rates up to the inflection point of untreated feedstock, and a, b and c are the parameters to be fitted, where b (= 163.9566) equals the optimum temperature, a (= 1.0612) affects the maximum height of the peak, and c (= 0.1403) denotes the width of the peak. Further, it was calculated that considerable effects of TBH need a minimum temperature of 115°C. At temperatures above 180°C the regression does not reflect all effects of TBH and overestimates the K-value at 220°C. Thus, it can be assumed that the regression refers more to the development of free carbon than to the formation of inhibitors, as already discussed above.

4.2. Transfer of lab-scale results in full-scale model

The results of lab-scale experiments, namely the

- fresh matter related organic matter content (Table 2 and Table 4) and
- the methane yields of the respective feedstocks before and after thermobarical hydrolysis (Table 7)

were used as input parameters of the full-scale model. As treatment at 180°C or lower was identified to show the strongest positive effect on methane yield in every case, results from treatment at higher temperatures are not regarded. The mixtures of SCM and de-ionized water were analyzed in lab-scale for assessing synergetic or antagonistic effects only, and

were not transferred to full-scale model. All other input parameters are gained from literature or from an unpublished engineering report (Table 6).

The fresh matter volume-flow of feedstock and maize silage substituted and the numbers of additional or reduced wheel loader trips per day calculated according to equation 1 are shown in Table 8.

Table 8: Parameters of untreated and treated feedstock and number of wheel loader trips

raw material	set-point temperature	mass fraction of methane from SCM in methane from SLCM	fresh matter related methane yield of		volume flow of		number of wheel loader trips
			LCM	SCM	MS	SCM	
	(°C)		($l_N \cdot kg^{-1}$ FM)		($m^3 \cdot d^{-1}$)		($trips \cdot d^{-1}$)
P1-LCM	untreated	-	-	-	-	-	-
P1-LCM	140	-	7.3	0.0	3.3	0.0	-4
P1-LCM	160	-	7.7	0.0	3.4	0.0	-4
P1-LCM	180	-	2.2	0.0	1.0	0.0	-1
P1-SCM	untreated	-	-	-	-	-	-
P1-SCM	140	-	0.0	29.2	10.4	12.0	1
P1-SCM	160	-	0.0	29.4	10.5	12.0	1
P1-SCM	180	-	0.0	33.9	12.1	12.0	-1
P1-SLCM	untreated	0.467	-	-	-	-	-
P1-SLCM	140	0.393	4.8	9.4	2.5	4.5	2
P1-SLCM	160	0.391	4.6	9.2	2.5	4.5	2
P1-SLCM	180	0.495	2.1	11.6	2.0	4.5	3
P2-LCM	untreated	-	-	-	-	-	-
P2-LCM	140	-	2.1	0.0	0.9	0.0	-1
P2-LCM	160	-	2.2	0.0	1.0	0.0	-1
P2-LCM	180	-	1.2	0.0	0.6	0.0	-1
P2-SCM	untreated	-	-	-	-	-	-
P2-SCM	140	-	0.0	39.2	14.0	12.0	-2
P2-SCM	160	-	0.0	43.2	15.4	12.0	-4
P2-SCM	180	-	0.0	29.9	10.6	12.0	1

LCM – Liquid cattle manure; MS – Maize silage; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SLCM – Solid and liquid cattle manure

4.3. Full-scale model and assessment

4.3.1. Energy balance of thermobarical pretreatment

The energy input for TBH construction is 18,730 $kWh_{el} \cdot a^{-1}$ or 4.5 or 5.6 $kWh_{el} \cdot Mg^{-1}$ if related to fresh matter mass (Table 9).

Table 9: Energetic assessment including energy payback time and energy payback mass

raw material	set-point temperature	P_{constr}	$P_{el,in}$	$P_{th,FS}$	$P_{th,process}$	P_{MC}		$P_{el,out}$		$P_{th,out}$	δP_{MS}	EPBT
						LCM	SCM	LCM	SCM			
	(°C)	($kWh \cdot a^{-1}$)										(P[n]Y[n]M)
P1-LCM	140	18,730	42,000	612,500	490,000	308,498	-	119,389	-	144,685	19,341	P4Y10M
P1-LCM	160	18,730	42,000	710,500	588,000	322,857	-	124,945	-	151,420	20,241	P4Y6M
P1-LCM	180	18,730	42,000	808,500	686,000	94,436	-	36,547	-	44,290	5,921	-
P1-SCM	140	18,730	42,000	490,000	392,000	-	980,265	-	379,362	459,744	61,457	P1Y1M
P1-SCM	160	18,730	42,000	568,400	470,400	-	987,062	-	381,993	462,932	61,883	P1Y1M
P1-SCM	180	18,730	42,000	646,800	548,800	-	1,139,986	-	441,175	534,654	71,470	P11M
P1-SLCM	140	18,730	42,000	612,500	490,000	202,105	394,995	78,214	152,863	280,040	37,435	P2Y
P1-SLCM	160	18,730	42,000	710,500	588,000	193,797	386,303	74,999	149,499	272,067	36,369	P2Y1M
P1-SLCM	180	18,730	42,000	808,500	686,000	87,794	486,492	33,976	188,273	269,340	36,004	P2Y1M
P2-LCM	140	18,730	42,000	612,500	490,000	86,406	-	33,439	-	40,524	5,417	-
P2-LCM	160	18,730	42,000	710,500	588,000	93,778	-	36,292	-	43,982	5,879	-
P2-LCM	180	18,730	42,000	808,500	686,000	52,138	-	20,177	-	24,453	3,269	-
P2-SCM	140	18,730	42,000	490,000	392,000	-	1,316,902	-	509,641	617,627	82,562	P10M
P2-SCM	160	18,730	42,000	568,400	470,400	-	1,452,106	-	561,965	681,038	91,038	P9M
P2-SCM	180	18,730	42,000	646,800	548,800	-	1,004,477	-	388,733	471,100	62,975	P1Y1M

raw material	set-point temperature	e_{constr}	$e_{el,in}$	$e_{th,FS}$	$e_{th,process}$	e_{MC}		$e_{el,out}$		$e_{th,out}$	δe_{MS}	EPBM
						LCM	SCM	LCM	SCM			
	(°C)	($kWh \cdot Mg^{-1}$ FM)										(Mg FM)
P1-LCM	140	4.5	10.0	145.8	116.7	73.5	-	28.4	-	34.4	4.6	20,330
P1-LCM	160	4.5	10.0	169.2	140.0	76.9	-	29.7	-	36.1	4.8	18,968
P1-LCM	180	4.5	10.0	192.5	163.3	22.5	-	8.7	-	10.5	1.4	-
P1-SCM	140	5.6	12.5	145.8	116.7	-	291.7	-	112.9	136.8	18.3	3,731
P1-SCM	160	5.6	12.5	169.2	140.0	-	293.8	-	113.7	137.8	18.4	3,702
P1-SCM	180	5.6	12.5	192.5	163.3	-	339.3	-	131.3	159.1	21.3	3,153
P1-SLCM	140	4.5	10.0	145.8	116.7	48.1	94.0	18.6	36.4	66.7	8.9	8,321
P1-SLCM	160	4.5	10.0	169.2	140.0	46.1	92.0	17.9	35.6	64.8	8.7	8,621
P1-SLCM	180	4.5	10.0	192.5	163.3	20.9	115.8	8.1	44.8	64.1	8.6	8,729
P2-LCM	140	4.5	10.0	145.8	116.7	20.6	-	8.0	-	9.6	1.3	-
P2-LCM	160	4.5	10.0	169.2	140.0	22.3	-	8.6	-	10.5	1.4	-
P2-LCM	180	4.5	10.0	192.5	163.3	12.4	-	4.8	-	5.8	0.8	-
P2-SCM	140	5.6	12.5	145.8	116.7	-	391.9	-	151.7	183.8	24.6	2,691
P2-SCM	160	5.6	12.5	169.2	140.0	-	432.2	-	167.3	202.7	27.1	2,421
P2-SCM	180	5.6	12.5	192.5	163.3	-	299.0	-	115.7	140.2	18.7	3,630

e_{constr} – Energy for construction of thermobarical hydrolysis device; $e_{el,in}$ – Electricity consumption of thermobarical hydrolysis device; $e_{el,out}$ – Electric energy attainable from the respective feedstock; e_{MC} – Methanation capacity; EPBT – Energy payback time; EPBM – Energy payback mass; $e_{th,FS}$ – Thermal power necessary for heating feedstock; $e_{th,out}$ - Thermal energy attainable from the respective feedstock; $e_{th,process}$ – Thermal energy flow from feedstock to biogas plant; LCM – Liquid cattle manure; P1 – Plant 1; P2 – Plant 2; P_{constr} – Energy for construction of thermobarical hydrolysis device; $P_{el,in}$ – Electricity consumption of thermobarical hydrolysis device; $P_{el,out}$ – Electric energy attainable from the respective feedstock; P_{MC} – Methanation capacity; $P_{th,FS}$ – Thermal power necessary for heating feedstock; $P_{th,out}$ - Thermal energy attainable from the respective feedstock; $P_{th,process}$ – Thermal energy flow from feedstock to biogas plant; SCM – Solid cattle manure; SLCM – Solid and liquid cattle manure

The energy input accounts for between 2.15 and 3.40 % of the overall energy demand (thermal as well as electric). The operation of the TBH demands much more energy, electric as well as thermal. The annual electric energy demand amounts to 42,000 $kWh_{el} \cdot a^{-1}$ and is needed for stirring and the thermal-oil pump, independently of the kind of feedstock. Related to fresh mass values are either 10 or 12.5 $kWh_{el} \cdot Mg^{-1}$ FM depending on feedstock bulk density of 1,000 or 800 $kg \cdot m^{-3}$ respectively. The electric energy demand presented here is comparable to values presented by Mönch-Tegeder et al. (2014) who needed 11.3 $kWh_{el} \cdot Mg^{-1}$ FM for mechanically pretreating horse manure in full-scale application and by Elbeshbishy et al. (2011) who calculated 13 $kWh_{el} \cdot Mg^{-1}$ FM for ultrasonic pretreatment. It accounts for between 4.83 and 7.63 % of the total energy demand of the TBH device. Thermal energy input required for achieving the treatment temperature also depends on the kind of feedstock, expressed in different densities. It ranges from 490,000 to 808,500 $kWh_{th} \cdot a^{-1}$ or 145.8 to 192.5 $kWh_{th} \cdot Mg^{-1}$ FM, accounting for roughly 90 % of the overall energy demand. Between 392,000 and 686,000 $kWh_{th} \cdot a^{-1}$ or 116.7 to 163.3 $kWh_{th} \cdot Mg^{-1}$ FM of this energy are available as process energy to maintain mesophilic conditions in the digester. It is estimated that this thermal process energy contributes to the thermal energy needed to maintain a mesophilic temperature in the digester under German ambient conditions for most of the year. The difference in energy values of TBH heat input and output to digester is caused by the different temperatures of feedstock before TBH treatment and substrate in the digester (15°C to 40°C). Consequently, the thermal energy actually required for hydrolysis is negligible.

The energy output of the TBH treatment of the different feedstocks is expressed as methanation capacity and is therefore independent of the overall conversion route of the methane. It can be divided into electric and thermal output, as well as losses if particular CHP is considered as conversion. The methanation capacity depends on feedstock and methane attainable as a consequence of differences in pretreatment. It ranges from 52,138 to 1,452,106 $kWh \cdot a^{-1}$. Considering a model CHP (Table 6), an electric energy output of 20,177 to 561,965 $kWh_{el} \cdot a^{-1}$ can be achieved. Thus, TBH-treated feedstock would contribute 0.7 to 20.3 % of the electric output of the CHP. The thermal output of the CHP from pretreated feedstock ranges from 24,453 to 681,038 $kWh_{th} \cdot a^{-1}$. A (surplus) energy output from 4.8 to 167.3 $kWh_{el} \cdot Mg^{-1}$ FM and 5.8 to 202.7 $kWh_{th} \cdot Mg^{-1}$ FM can be gained via the conversion route methane – CHP. Thus, the electricity input for thermobarical treatment accounts for 7 % of the electricity output in best case and 208 % in worst case.

An increase in uncoupled thermal energy from CHP is possible by cooling down the exhaust gas to 180°C, as during the first period of heat-up the heat input into feedstock is limited by the available thermal power. Above a feedstock temperature of approximately 110°C, the heat input into feedstock is limited by the heat transfer that is lower than the thermal power

available. It should be possible to considerably enhance the thermal power used by operating two devices time off-set in parallel during this second period. Thus, the share of alternative feedstock can be significantly enhanced.

The electric energy possibly gained depends on feedstock and changes in digestibility as well as on the organic matter (OM (in % FM)) of feedstock. Feedstock with high OM and hence higher FM-related methane yield is preferred as the fixed vessel volume limits the fresh matter volume to be pretreated per batch. In the case of P1-LCM pretreated at 180°C and all variants of P2-LCM, the electricity consumption is higher than the electricity produced. But compared with alternative pretreatment methods the electric energy consumption is very low: e.g. an extruder sized for the same mass flow will need approximately 20 kW_{el} and will cause much higher costs for maintenance and spare parts (Weiß & Brückner, 2008).

From an energetic point of view, it is possible to obtain more thermal energy from pretreated feedstock than is necessary for pretreatment, e.g. P2-SCM pretreated at 140 and 160°C deliver 617,627 and 681,038 $kWh_{th} \cdot a^{-1}$, but need only 490,000 and 568,400 $kWh_{th} \cdot a^{-1}$ respectively. From the exergetic point of view, the balance may be inversed. Only 96.3 kW (24.1 % of nominal thermal power) are transferred to feedstock through TBH from 158 kW thermal power (that is 39.5 % of the nominal thermal power of the CHP) uncoupled from CHP exhaust gas.

Substituting maize silage as biogas feedstock can save between 3,269 and 91,038 $kWh \cdot a^{-1}$, thus enhancing the “fuel” output (P_{MC}) by 6.3 % in any case.

The lowest energy payback time is 9 months. Although only the extra amount of methane from LCM is included in the calculation, it is possible to reach an EPBT of 4 years 6 months. Compared with other renewable energy converting facilities, the EPBT can be very short. Wind turbines for example need 3 to 6 months, photovoltaic cells 2 to 5 years to feed in the electricity needed for construction (Lübbert, 2007). Related to fresh mass (EPBM) 2,421 to 20,330 Mg FM are to be pretreated in order to achieve the same amount of energy that was spent for construction of the TBH device. The annual volumetric throughput of 4,200 m³ FM equals 3,360 or 4,200 Mg FM, depending on bulk density. The energy payback time or mass in total is of course at least that of the biogas plant as the TBH device is only a pretreating unit attached to a biogas plant (including the CHP) that is the actual renewable energy converting facility.

4.3.2. Greenhouse gas emissions balance of thermobarical pretreatment

Thermobarical hydrolysis can save a considerable amount of greenhouse gases of up to 0.672 kg CO_2-eq.$\cdot kWh_{el}^{-1}$ or 377,504 kg CO_2-eq. per year (Table 10).

Table 10: Greenhouse gas emissions, greenhouse gas payback time, and greenhouse gas payback mass

raw material	set-point temperature	GHG_{constr}	$GHG_{el,in}$	δGHG_{SCM}	δGHG_{MS}	GHG_{net}	GHG_{net}	GPBT
	(°C)	(kg CO_2-eq.·kWh_{el}^{-1})					(kg CO_2-eq.·a^{-1})	(P[n]Y[n]M)
P1-LCM	140	0.0358	0.215	-	-0.2135	0.037	4,446	-
P1-LCM	160	0.0342	0.205	-	-0.2135	0.026	3,260	-
P1-LCM	180	0.1169	0.702	-	-0.2135	0.606	22,133	-
P1-SCM	140	0.0113	0.068	-0.512	-0.2135	-0.646	-245,112	P4M
P1-SCM	160	0.0112	0.067	-0.512	-0.2135	-0.647	-247,019	P4M
P1-SCM	180	0.0097	0.058	-0.512	-0.2135	-0.657	-289,928	P4M
P1-SLCM	140	0.0185	0.111	-0.271	-0.2135	-0.355	-81,954	P1Y1M
P1-SLCM	160	0.0190	0.114	-0.273	-0.2135	-0.353	-79,173	P1Y1M
P1-SLCM	180	0.0192	0.115	-0.347	-0.2135	-0.425	-94,560	P11M
P2-LCM	140	0.1278	0.767	-	-0.2135	0.682	22,796	-
P2-LCM	160	0.1178	0.707	-	-0.2135	0.611	22,187	-
P2-LCM	180	0.2118	1.272	-	-0.2135	1.270	25,628	-
P2-SCM	140	0.0084	0.050	-0.512	-0.2135	-0.666	-339,568	P3M
P2-SCM	160	0.0076	0.046	-0.512	-0.2135	-0.672	-377,504	P3M
P2-SCM	180	0.0110	0.066	-0.512	-0.2135	-0.648	-251,906	P4M

raw material	set-point temperature	$GHG^{‡}_{constr}$	$GHG^{‡}_{el,in}$	$\delta GHG^{‡}_{SCM}$	$\delta GHG^{‡}_{MS}$	$GHG^{‡}_{net}$	GPBM
	(°C)	(kg CO_2-eq.·Mg^{-1} FM)					(Mg FM)
P1-LCM	140	1.0	6.1	-	-6.1	1.1	-
P1-LCM	160	1.0	6.1	-	-6.4	0.8	-
P1-LCM	180	1.0	6.1	-	-1.9	5.3	-
P1-SCM	140	1.3	7.6	-57.8	-24.1	-73.0	1,172
P1-SCM	160	1.3	7.6	-58.2	-24.3	-73.5	1,163
P1-SCM	180	1.3	7.6	-67.2	-28.0	-86.3	991
P1-SLCM	140	1.0	6.1	-18.6	-11.7	-23.2	3,678
P1-SLCM	160	1.0	6.1	-18.2	-11.4	-22.5	3,800
P1-SLCM	180	1.0	6.1	-22.9	-11.3	-27.1	3,154
P2-LCM	140	1.0	6.1	-	-1.7	5.4	-
P2-LCM	160	1.0	6.1	-	-1.8	5.3	-
P2-LCM	180	1.0	6.1	-	-1.0	6.1	-
P2-SCM	140	1.3	7.6	-77.6	-32.4	-101.1	846
P2-SCM	160	1.3	7.6	-85.6	-35.7	-112.4	761
P2-SCM	180	1.3	7.6	-59.2	-24.7	-75.0	1,140

GHG_{constr} and $GHG^{‡}_{constr}$ – Emissions from construction of thermobarical hydrolysis device; $GHG_{el,in}$ and $GHG^{‡}_{el,in}$ – Emissions from electricity consumption of thermobarical hydrolysis; δGHG_{SCM} and $\delta GHG^{‡}_{SCM}$ – Emissions from storing SCM; δGHG_{MS} and $\delta GHG^{‡}_{MS}$ – Emissions from substitution of maize silage; GHG_{net} and $GHG^{‡}_{net}$ – Sum of all emissions; GPBT – Greenhouse gas payback time; GPBM – Greenhouse gas payback mass; LCM – Liquid cattle manure; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SLCM – Solid and liquid cattle manure

LCM does not save GHG emissions and emits from 0.026 to a maximum of 1.270 kg CO_2-eq.·kWh_{el}^{-1}.

The emissions from construction and operation of a TBH device related to electric energy output are affected by the fresh matter related methane yields of respective feedstock while the absolute emissions are independent of feedstock and treatment temperatures. The emissions from construction are 0.0076 to 0.2118 kg CO_2-eq.·kWh_{el}^{-1}, accounting for 14 % of all emissions (without regarding emissions mitigated) in any case. The complementary 86 % of emissions arise from grid electricity used for operation of the device and amount to 0.046 to 1.272 kg CO_2-eq.·kWh_{el}^{-1}.

The mitigation potential of using SCM is 0.512 kg CO_2-eq.·kWh_{el}^{-1} in any case, as both the saved CO_2 emissions and the electricity generated are directly dependent on methane production. It accounts for 71 % of the overall mitigations. The mitigation potential of SLCM derives from the share of SCM and is between 0.271 and 0.347 kg CO_2-eq.·kWh_{el}^{-1}, accounting for between 56 and 62 %.

LCM does not mitigate GHG emissions, as it is assumed that thermobarical pretreatment releases feedstock constituents that – without pretreatment – would not have contributed to methane emissions during storage of untreated LCM because of their lower degradability.

When maize silage is substituted, further GHG emissions of 0.2135 kg CO_2-eq.·kWh_{el}^{-1} can be avoided. These include the entire supply chain as well as direct land use changes. This avoidance contributes to the overall mitigation by 100 % in the case of LCM, 29 % in the case of SCM, and 38 to 44 % in the case of SLCM. The differences in relative mitigation are mainly attributable to the differences in SCM storage and their emission mitigation.

The net emissions of TBH treatment can be as low as 7 % of the total mitigated emissions, or exceed them by 595 %. SCM and SLCM save emissions in any case. The highest value of emissions is 11 % of mitigated emissions for SCM and 27 % for SLCM. LCM always emits more GHG than are mitigated. The relative values range from 112 to 695 %.

The differences between the various scenarios become even more obvious if mitigation effect per year is considered. The values range from -377,504 to 25,628 kg CO_2-eq.·a^{-1}. For example, P1-SLCM treated at 160°C compared with P2-SCM treated at 160°C differ in energy-related GHG emissions from -0.353 kg CO_2-eq.·kWh_{el}^{-1} to -0.672 kg CO_2-eq.·kWh_{el}^{-1}, while the annual emissions vary more than 4-fold with values of -79,173 kg CO_2-eq.·a^{-1} and -377,504 kg CO_2-eq.·a^{-1} respectively. The difference in energy related emissions is mainly caused by mitigation potential of the various feedstocks while the time-related value is further amplified by the much higher fresh matter related methane yield of SCM compared with SLCM or LCM.

Treatment temperature further controls the mitigation potential. Appropriate treatment can lead to 50 % higher GHG omissions per year, e.g. SCM from P2 pretreated at 160°C with a daily input of 12 m³ saves 377,504 CO_2-eq. per year, whereas when pretreated at 180°C, with even a higher methane yield than the untreated SCM, it saves only 251,906 kg CO_2-eq.·a^{-1}. In most cases, 160°C is the optimal pretreatment temperature.

The potentials described above directly influence the greenhouse gas payback time. The GPBT of a TBH device using SCM is very short, between 3 and 4 months. Pretreating SLCM leads to a GPBT of between 11 and 13 months. LCM does not have any GPBT because emissions always exceed mitigation. Related to fresh mass a substantial amount of between 22.5 and 112.4 kg CO_2-eq.·Mg^{-1} FM can be omitted by implementing a TBH device in an already existing biogas plant. The GPBM ranges from 761 to 3,800 Mg FM.

4.3.3. Profitability and mitigation costs of thermobarical pretreatment

The annual profits range from 3,763 to 60,253 €·a^{-1} using SCM or SLCM as feedstock whereas LCM only generates costs of up to 23,199 €·a^{-1} (Table 11).

The cost items of TBH treatment comprise capital costs and depreciation of TBH, costs of operation and maintenance, costs of wheel loader employment and costs of spreading manure. The revenues derive from savings from alterations in wheel loader employment and spreading, substitution of maize silage (feedstock costs), as well as from the feedstock-specific bonus for selling electricity to the grid.

Depreciation and capital costs for the TBH device are responsible for two thirds of the overall costs and range from 3.11 to 86.73 ct·kWh_{el}^{-1}. Each, costs of electricity consumption and costs of maintenance and spare parts, account for a sixth of the overall costs, ranging from 0.75 to 22.90 ct·kWh_{el}^{-1}.

Additional wheel loader employment compared with the reference scenario costs up to 0.40 ct·kWh_{el}^{-1}. These costs have a 1 to 3 % share in the overall costs. Up to 1.47 ct·kWh_{el}^{-1} can be saved if wheel loader employment can be decreased, thus contributing 9 % to the revenues.

The electricity production costs can be reduced by a maximum of 3.78 ct·kWh_{el}^{-1} by changing the spreading procedure from solid manure to liquid digestate. The reduction in costs following substitution by LCM is up to 1.94 ct·kWh_{el}^{-1}. Saved spreading costs amount to approximately one eighth of the total revenue for LCM, 20 to 24 % for SCM, and 13 to 14 % for SLCM.

Table 11: Economic assessment including economic amortization period, economic amortization mass and CO_2 mitigation costs

raw material	set-point temperature	C_{constr}	$C_{el,in}$	C_{MT}	δC_{WL}	$\delta C_{spreading}$	$\delta C_{el,out}$	δC_{MS}	Profit	Profit	ECAP	CMC
	(°C)	($ct \cdot kWh_{el}^{-1}$)								($€ \cdot a^{-1}$)	(P[n]Y[n]M)	($€ \cdot Mg^{-1}$ CO_2-eq.)
P1-LCM	140	14.66	3.87	3.52	-0.99	-1.80	-2.00	-10.06	-7.19	-8,584	P28Y	200
P1-LCM	160	14.01	3.70	3.36	-0.95	-1.77	-2.00	-10.06	-6.28	-7,848	P25Y11M	180
P1-LCM	180	47.88	12.64	11.49	-0.81	-1.78	-2.00	-10.06	-57.36	-20,964	-	114,151
P1-SCM	140	4.61	1.22	1.11	0.08	-3.78	-2.00	-10.06	8.83	33,488	P4Y11M	-36
P1-SCM	160	4.58	1.21	1.10	0.08	-3.77	-2.00	-10.06	8.87	33,870	P4Y10M	-37
P1-SCM	180	3.97	1.05	0.95	-0.07	-3.50	-2.00	-10.06	9.67	42,644	P4Y2M	-43
P1-SLCM	140	7.57	2.00	1.82	0.26	-1.94	-2.00	-10.06	2.36	5,450	P10Y11M	20
P1-SLCM	160	7.80	2.06	1.87	0.26	-2.00	-2.00	-10.06	2.07	4,656	P11Y3M	23
P1-SLCM	180	7.87	2.08	1.89	0.40	-1.87	-2.00	-10.06	1.69	3,763	P11Y9M	25
P2-LCM	140	52.33	13.82	12.56	-0.88	-1.75	-2.00	-10.06	-64.01	-21,404	-	-
P2-LCM	160	48.22	12.73	11.57	-0.81	-1.80	-2.00	-10.06	-57.85	-20,994	-	-
P2-LCM	180	86.73	22.90	20.82	-1.47	-1.94	-2.00	-10.06	-114.98	-23,199	-	-
P2-SCM	140	3.43	0.91	0.82	-0.12	-3.27	-2.00	-10.06	10.29	52,438	P3Y7M	-47
P2-SCM	160	3.11	0.82	0.75	-0.21	-3.13	-2.00	-10.06	10.72	60,253	P3Y3M	-50
P2-SCM	180	4.50	1.19	1.08	0.08	-3.72	-2.00	-10.06	8.94	34,748	P4Y9M	-37

raw material	set-point temperature	$C^{‡}_{constr}$	$C^{‡}_{el,in}$	$C^{‡}_{MT}$	$\delta C^{‡}_{WL}$	$\delta C^{‡}_{spreading}$	$\delta C^{‡}_{el,out}$	$\delta C^{‡}_{MS}$	Profit‡	ECAM
	(°C)	(€·Mg^{-1} FM)								(Mg FM)
P1-LCM	140	4.17	1.10	1.00	-0.28	-0.51	-0.57	-2.86	-2.04	117,764
P1-LCM	160	4.17	1.10	1.00	-0.28	-0.53	-0.59	-2.99	-1.87	108,790
P1-LCM	180	4.17	1.10	1.00	-0.07	-0.16	-0.17	-0.88	-4.99	-
P1-SCM	140	5.21	1.38	1.25	0.09	-4.27	-2.26	-11.36	9.97	16,475
P1-SCM	160	5.21	1.38	1.25	0.09	-4.29	-2.27	-11.44	10.08	16,352
P1-SCM	180	5.21	1.38	1.25	-0.09	-4.60	-2.63	-13.21	12.69	13,966
P1-SLCM	140	4.17	1.10	1.00	0.14	-1.07	-1.10	-5.54	1.30	45,751
P1-SLCM	160	4.17	1.10	1.00	0.14	-1.07	-1.07	-5.38	1.11	47,390
P1-SLCM	180	4.17	1.10	1.00	0.21	-0.99	-1.06	-5.32	0.90	49,381
P2-LCM	140	4.17	1.10	1.00	-0.07	-0.14	-0.16	-0.80	-5.10	-
P2-LCM	160	4.17	1.10	1.00	-0.07	-0.16	-0.17	-0.87	-5.00	-
P2-LCM	180	4.17	1.10	1.00	-0.07	-0.09	-0.10	-0.48	-5.52	-
P2-SCM	140	5.21	1.38	1.25	-0.18	-4.97	-3.03	-15.26	15.61	12,011
P2-SCM	160	5.21	1.38	1.25	-0.35	-5.24	-3.35	-16.83	17.93	10,803
P2-SCM	180	5.21	1.38	1.25	0.09	-4.31	-2.31	-11.64	10.34	16,077

C_{constr} and $C^{‡}_{constr}$ – Costs of construction of thermobarical hydrolysis device; $C_{el,in}$ and $C^{‡}_{el,in}$ – Costs of electricity consumption of thermobarical hydrolysis device; $\delta C_{el,out}$ and $\delta C^{‡}_{el,out}$ – Costs of selling electricity; CMC – CO_2 mitigation costs; δC_{MS} and $\delta C^{‡}_{MS}$ – Costs of maize silage; C_{MT} and $C^{‡}_{MT}$ – Costs of maintenance of thermobarical hydrolysis device; $\delta C_{spreading}$ and $\delta C^{‡}_{spreading}$ – Costs of spreading manure or digestate; δC_{WL} and $\delta C^{‡}_{WL}$ – Costs of feedstock transport by wheel loader; ECAP – Economic amortization period; ECAM – Economic amortization mass; LCM – Liquid cattle manure; P1 – Plant 1; P2 – Plant 2; SCM – Solid cattle manure; SLCM – Solid and liquid cattle manure

Although methane yields of the feedstock examined differ from the statutory values, the fee attainable is fixed at 2 cent per kWh_{el} in each case. In general, it can be stated that a methane yield higher than the statutory level is assumed to lower the share of energy crops in total feedstock to achieve the same electric power and therefore increases the fee attainable and consequently the income. This applies for LCM from plant 1 pretreated at 140 and 160°C only. The income assigned to this bonus contributes 13 to 14 % to the total revenues.

If related to fresh mass, the revenues are between 0.65 and 22.42 €·Mg^{-1} FM disregarding additional income from feed-in fees according to the Renewable Energy Sources Act (German Government, 2012a) which range from 0.10 to 3.35 €·Mg^{-1} FM.

The overall electricity production costs, disregarding saved expenditures for maize silage and additional income due to Renewable Energy Sources Act, range from 1.34 ct·kWh_{el}^{-1} to 127.04 ct·kWh_{el}^{-1}. These values allow the feedstock regarded to be assessed under differing legal or economic circumstances. They demonstrate that TBH pretreatment is feasible as long as feedstock substituted costs more than 1.34 ct·kWh_{el}^{-1}. Considering all possible revenues, the total electricity production costs would be negative and amount to -0.66 ct·kWh_{el}^{-1} in the best case. Related to the targeted electricity production costs of 10.06 ct·kWh_{el}^{-1} – that are the costs of maize silage, feedstock to be substituted – these overall costs are within a very wide range: between -107 and 1243 %. The LCM variants have a negative profit and are not economically viable. The profits of the other variants range from 1.69 to 10.72 ct·kWh_{el}^{-1}. Moreover, the energy-related values are here amplified by the methanation capability of the respective feedstock. The annual profits are then between 3,763 and 60,253 €·a^{-1}. If related to fresh mass, the total costs amount for 2.24 to 6.10 €·Mg^{-1} FM. Cano et al. (2014) presented costs for construction of a steam explosion facility of 3.33 €·Mg^{-1} FM, if considered a mass flow of 30,000 Mg FM·a^{-1}. These costs are higher compared to 2.98 €·Mg^{-1} FM for construction of a TBH device at a mass flow of 4,200 Mg FM·a^{-1} and although lower than 3.72 €·Mg^{-1} FM at a mass flow of 3,360 Mg FM·a^{-1} it is assumed that they are higher in any case if regarding the economy of scale.

The ECAP lies between 3 years and 3 months in the best case (P2-SCM; 160°C) and 28 years in the worst case (P1-LCM; 140°C). Most feedstocks, but none of the LCM variants, are economically feasible as the device is designed for a service life of 20 years. The fresh mass to be pretreated for regaining the entire investment (ECAM) is between 10,803 and 117,764 Mg FM.

If the additional electricity production costs according to this study are lower than the grid electricity production costs, the additional CO_2 mitigation costs become negative. The CO_2 mitigation costs of the process step regarded would result in -50 €·Mg^{-1} CO_2-eq. in the best case, thus reducing the CO_2 mitigation costs of electricity in biogas plant. These costs

usually range between 350 €·Mg^{-1} CO_2-eq. for biogas plants using a substantial share of LCM and 600 €·Mg^{-1} CO_2-eq. for biogas plants using energy crops only (Scholz, et al., 2011).

4.3.4. Sensitivity analysis

Sensitivity analyses were performed to assess the viability of the model against hardly determinable parameters, to justify simplifications and to assess the impact of variations of selected input parameters on representative output parameters.

GHG emissions per unit energy increase with increasing stirring power (Figure 9), decrease with increasing organic matter content (Figure 10) and are indifferent to changes in investment (not shown here).

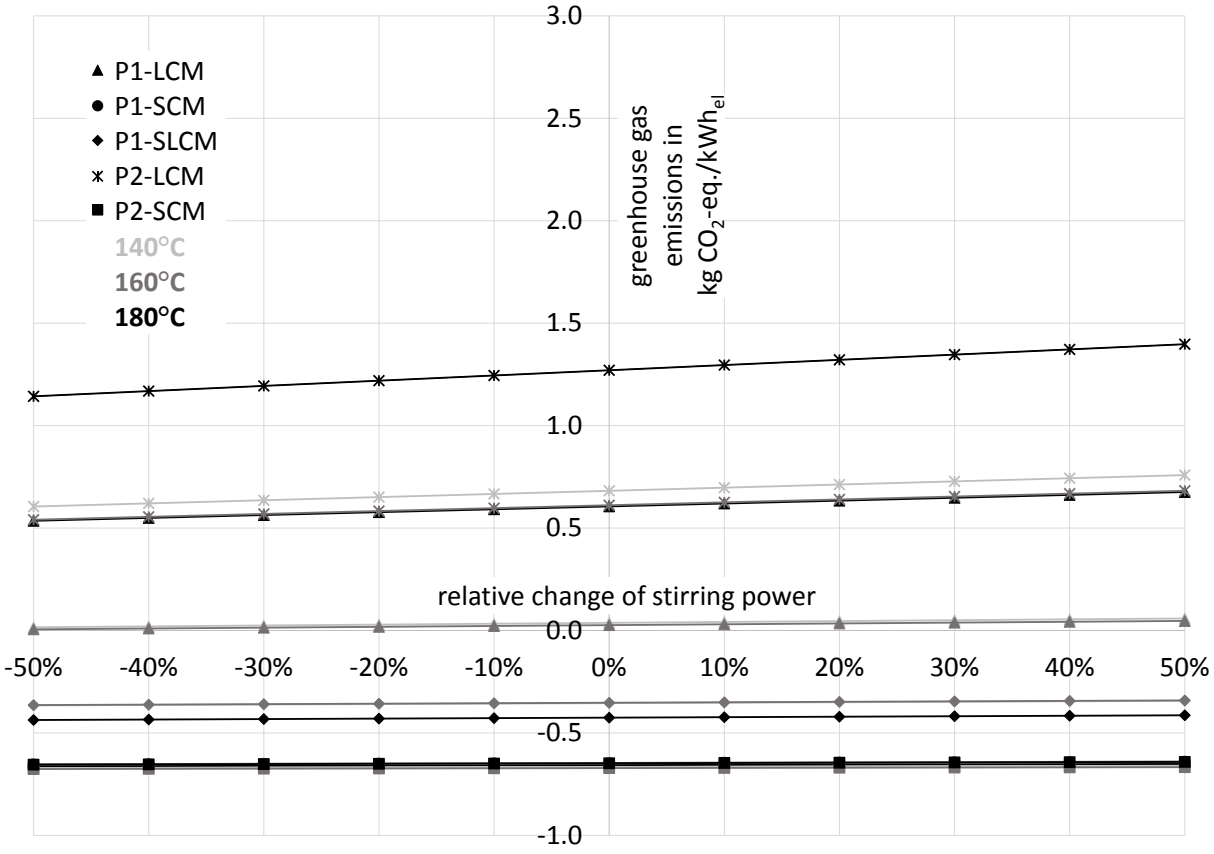

Figure 9: Sensitivity analysis of the influence of changes in stirring power on GHG emissions

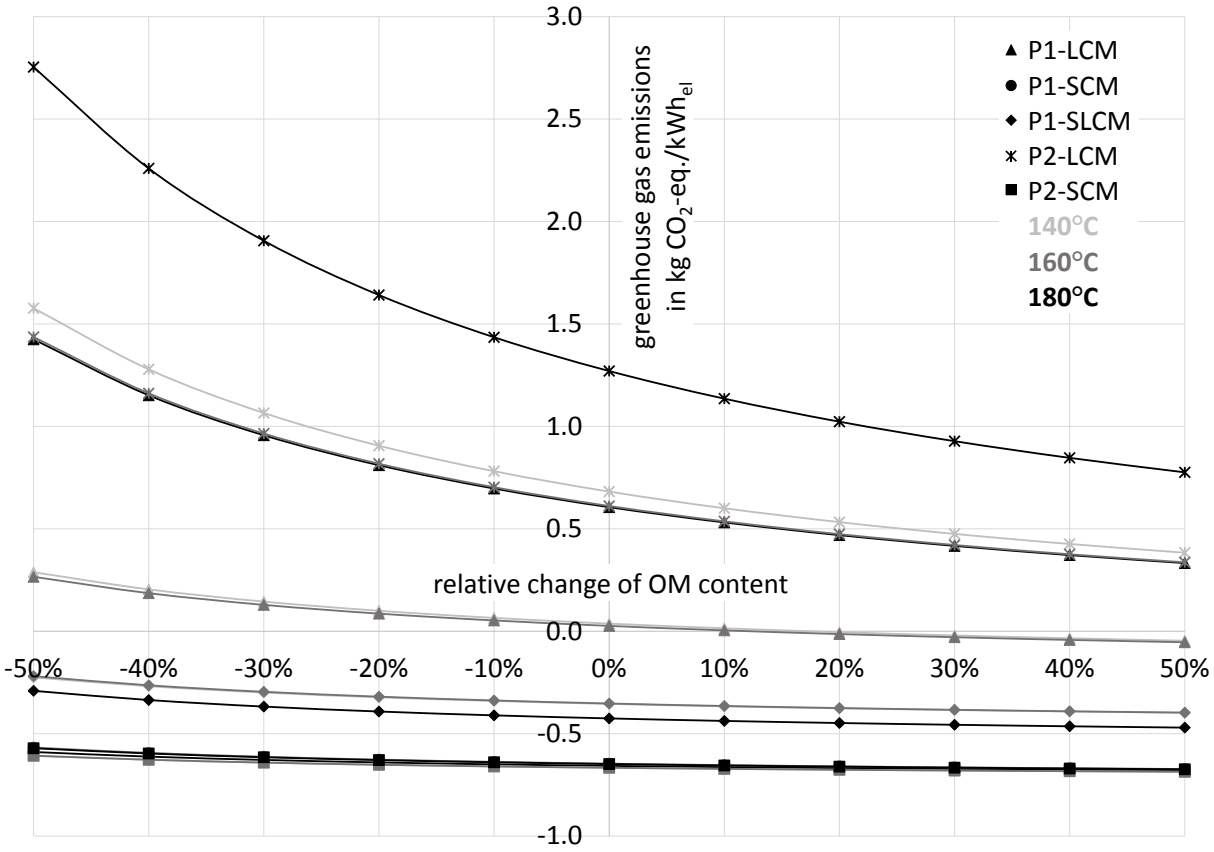

Figure 10: Sensitivity analysis of the influence of changes in OM content on GHG emissions in terms of kg CO_2-eq.·kWh_{el}^{-1}

The increase in GHG emissions with increasing stirring power is due to the fact that the electricity used here derives from the national grid with its fossil and nuclear resources. The alteration of stirring power from -50 or +50 % leads to changes in GHG emissions of maximum 0.127 kg CO_2-eq.·kWh_{el}^{-1}.

OM content of the particular feedstock has a considerably stronger impact on GHG emissions than the changes in stirring power. The alteration of OM content of - 50 % leads to an increase of maximum 1.484 kg CO_2-eq.·kWh_{el}^{-1} while the increase in OM content by 50 % leads to a decrease of maximum 0.495 kg CO_2-eq.·kWh_{el}^{-1}. Owing to the increasing amount of maize silage displaced with increasing OM content, the GHG emissions of LCM scenarios decrease. Increasing OM content in SCM scenarios omits surplus emissions from storage and hence decreases the net value GHG emissions.

Although the effect of OM content of a particular feedstock is non-linear and almost doubles the GHG emissions per unit energy with a decrease of 50 % in the OM content of LCMs, the impact on GHG emission per year is negligible for LCMs (Figure 11). On the other hand, the GHG emissions per year from SCM scenarios decrease considerably with increasing OM content of the feedstock. These differences reflect the increasing yield in surplus energy deriving from feedstock with higher OM content like SCMs.

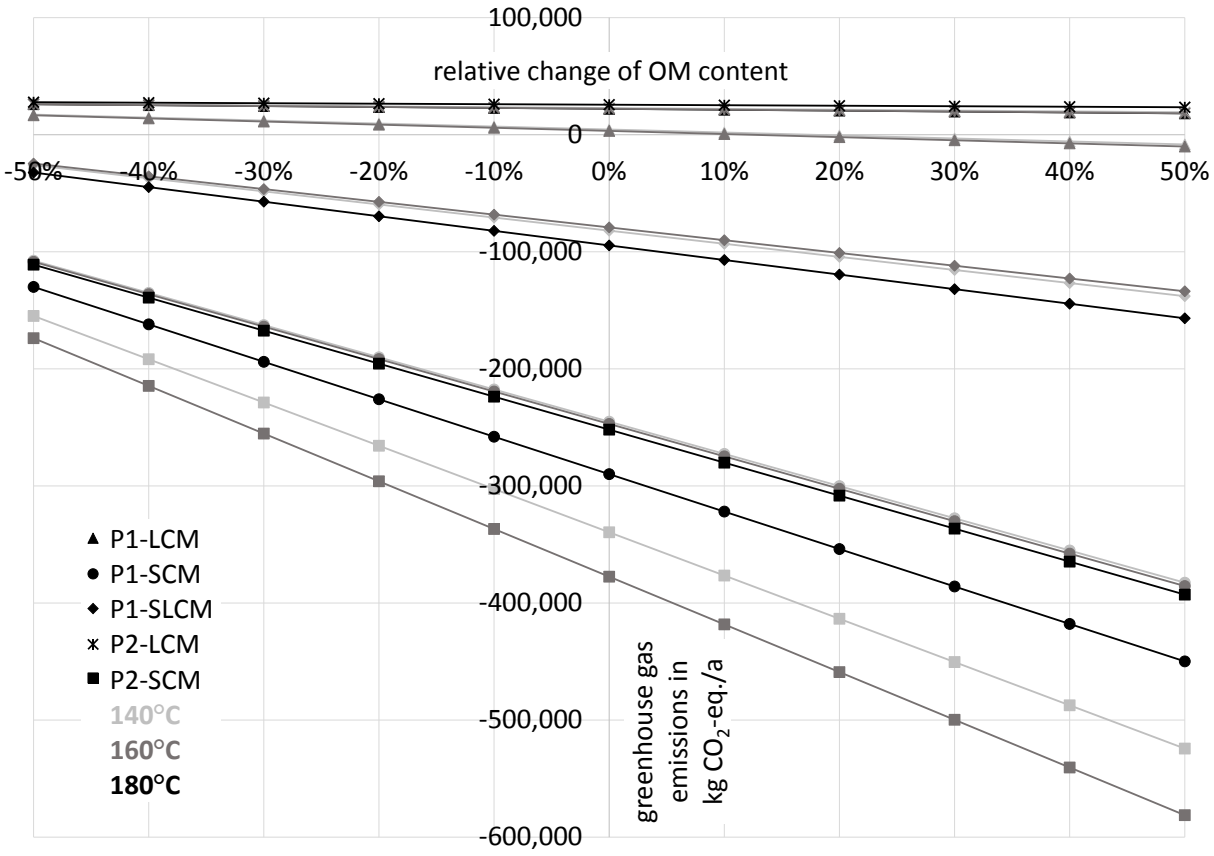

Figure 11: Sensitivity analysis of the influence of changes in OM content on GHG emissions in terms of kg CO_2-eq.·a^{-1}

CO_2 mitigation costs are significantly decreased by increasing OM content of feedstock (Figure 12) but are almost unaffected by changes in stirring power (not displayed here). Investment is directly influencing linearly the CMCs (not displayed here).

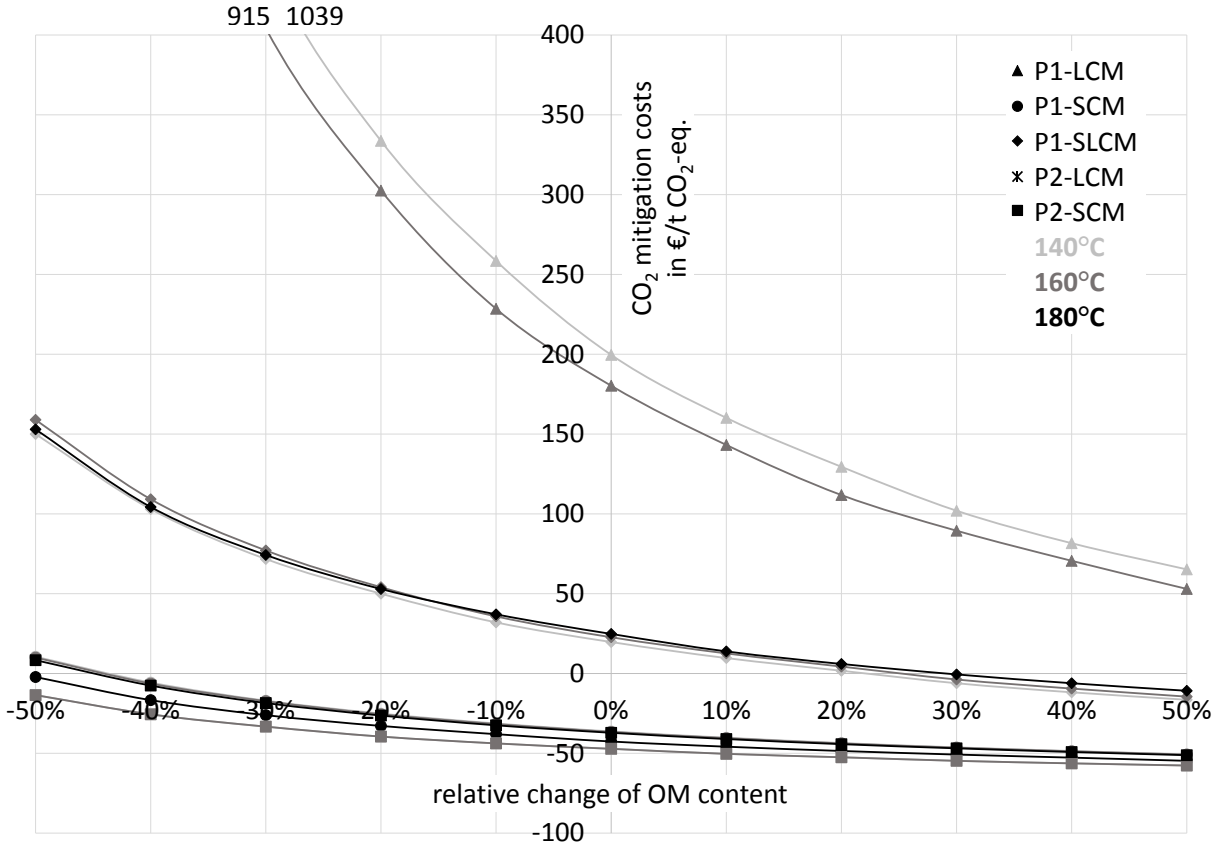

Figure 12: Sensitivity analysis of the influence of changes in OM content on CO_2 mitigation costs

Scenarios with high electricity production costs and high energy related emissions compared to that of grid electricity in base scenario are strongly influenced by changes in OM content. As shown above, increase in OM content reduces the emissions related to electric energy and reduces the costs for producing that electric energy as well. Especially the CMCs of LCM scenarios are therefore significantly decreased by increased OM content. SLCM also shows a sixfold increase with decrease of the OM content of feedstock by 50 %. The SCMs are slightly reduced by decrease of OM content and almost unaffected by increase.

Sensitivity analyses for the ECAP display a baseline (x-axis) at the specified lifetime of the TBH facility of 20 years or 240 months (Figure 13 to Figure 15).

Stirring power only slightly influences the ECAP (Figure 13). The maximal change in the ECAP within lifetime of the TBH facility is from 135 months for the original scenario to 130 months for -50 % and to 138 months for +50 % stirring power. That is a change of 5.7 % only.

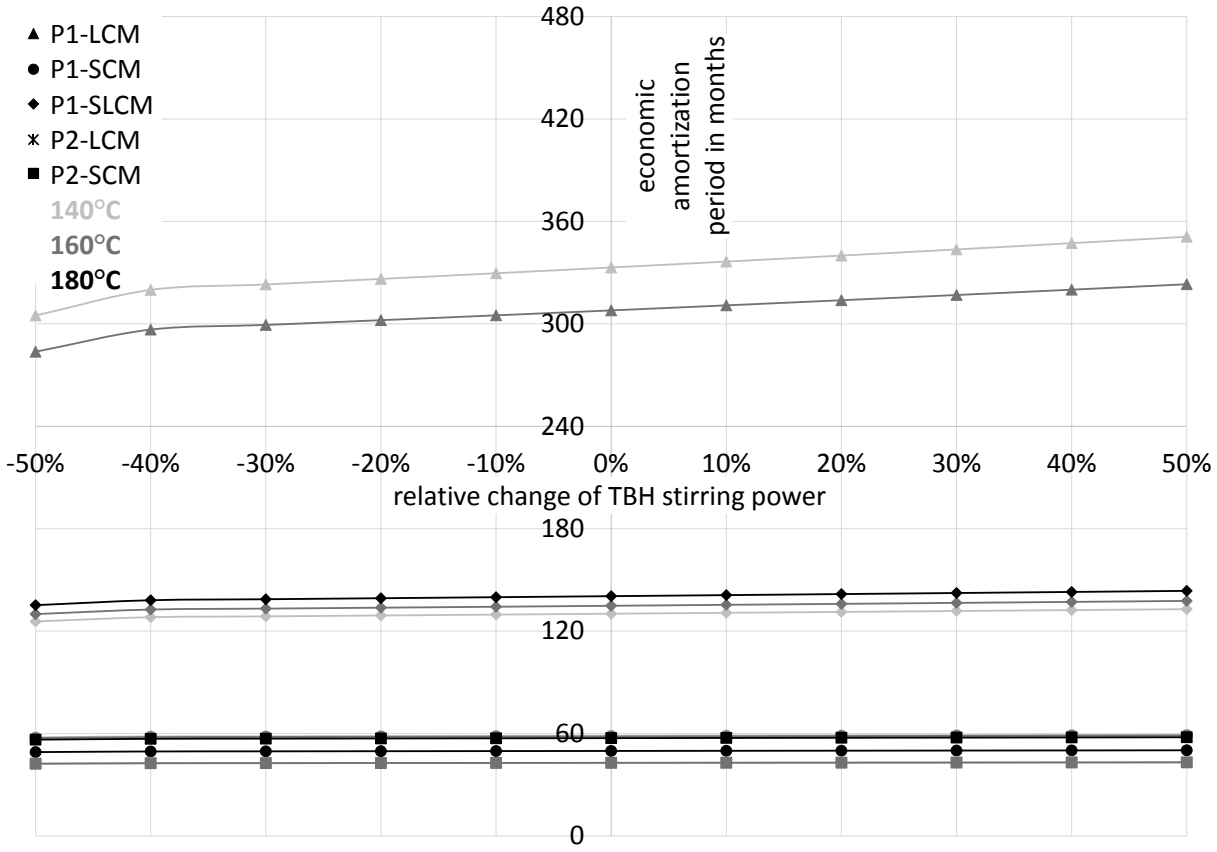

Figure 13: Sensitivity analysis of the influence of changes in stirring power on the economic amortization period

In contrast, changes in OM content strongly influence the ECAP (Figure 14). In the case of LCM from P1 pretreated at 140°C, 15 € per year only can be gained for paying off the investment if the OM content is decreased by 50 %. That leads to an irrelevantly high ECAP of approximately 16,000 years. On the other hand, however, an increase in OM content by 50 % leads to an amortization of investment after 172 months which is within the specified lifetime of the TBH facility. The SCMs show an increase of the ECAP of 60 months in average with decreasing OM content by 50 % and a decrease of 18 months in average with an increase of the OM content of 50 %.

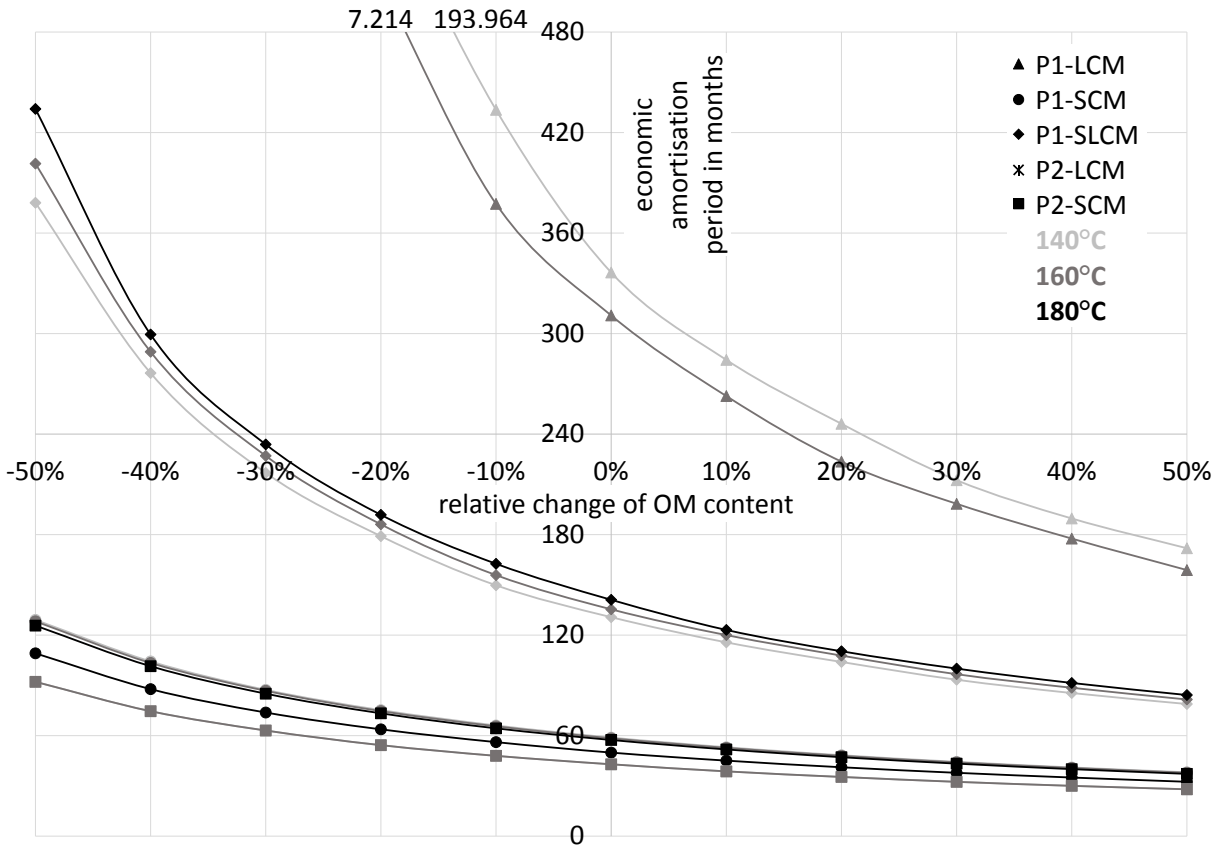

Figure 14: Sensitivity analysis of the influence of changes in OM content on the economic amortization period

Investment significantly influences the ECAP (Figure 15). This is given especially for variants with profits above the interest rate and below the repayment rate as for P1-LCM pretreated at 140 and 160°C. Absurdly high values occur here as well: The ECAP for P1-LCM pretreated at 140°C is 1,500 years if investment is increased by 50 %. Variants with only low profit are also strongly influenced: A surplus in investment of 50 % causes a doubling of ECAP for P1-SLCM. In contrast, variants with already high profits are more or less unimpaired by changes in investment as it is given for the SCM scenarios.

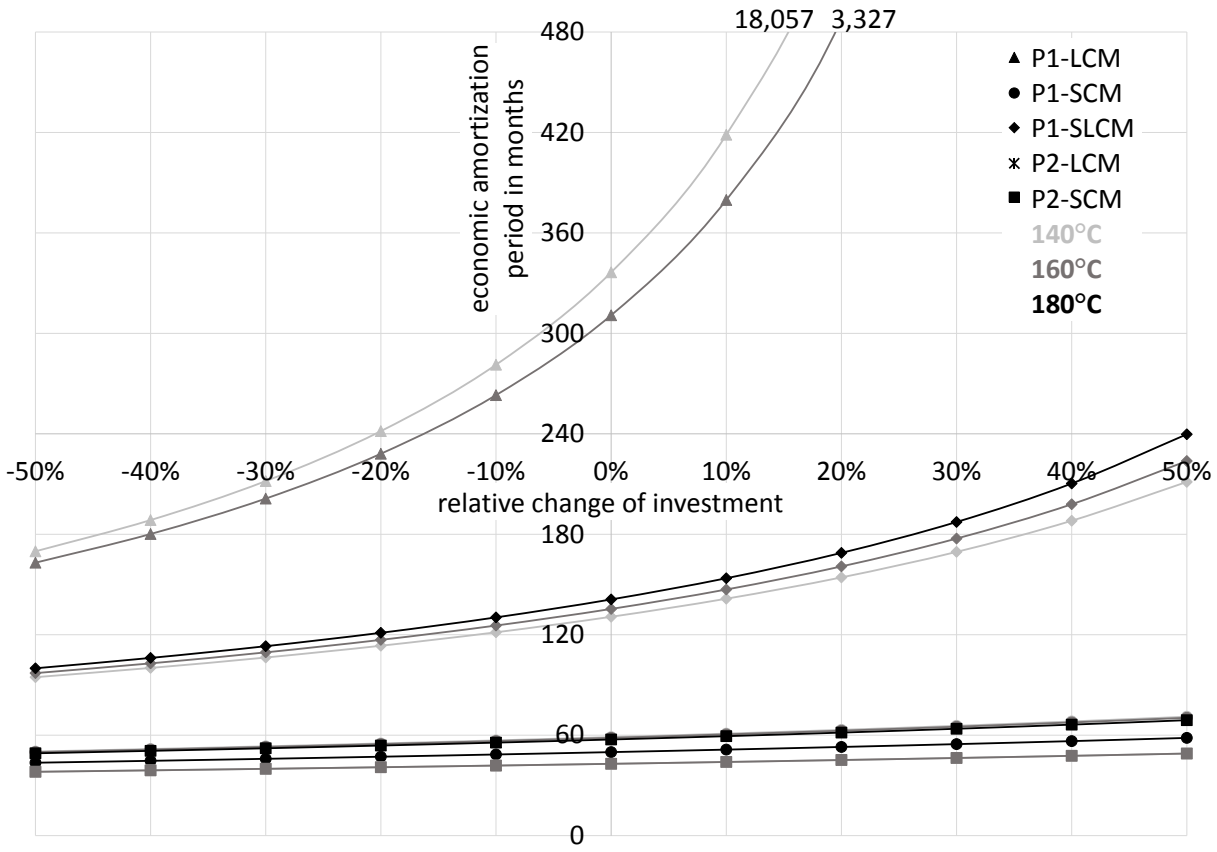

Figure 15: Sensitivity analysis of the influence of changes in investment on the economic amortization period

The performed sensitivity analyses confirm the assumption that the overall results are influenced only marginally by the accuracy of estimating the stirring power.

Only slight changes in output parameters occur if related to time as the energy per time unit of LCM is low. However, if related to energy they are leading to substantial changes of the overall results. In opposition to the LCMs, the energy per time unit attainable from SCMs is – in contrast to the changes in energy related output parameters – high.

Conclusions

Thermobarical treatment leads to increased degradation of lignocellulosic waste and hence to increased availability of digestible substances. The extended analysis proves that thermobarical treatment affects mainly the hydrolysis phase of anaerobic digestion. It can also be concluded that thermobarical hydrolysis displays performance superior to that of biological hydrolysis. The improved hydrolysis enhances several factors of anaerobic digestion, e.g. decrease in stirring power due to lower viscosity and significantly increased methane yields. The decreased stirring power as well as the separation of solid and liquid fractions of feedstock observed after thermobarical hydrolysis allows the conclusion that the formation of swimming layers in downstream biogas plant digesters will be avoided or at least reduced. The formation of inhibitors and non-digestible substances such as free carbon has a considerable negative impact on methane yield at treatment temperatures above 180°C. Further research is needed to clarify the dependency of differences in feedstock properties on methane yields before and after thermobarical hydrolysis conclusively.

Thermobarical hydrolysis is feasible for feedstocks rich in lignocellulose and with sufficient high organic matter content such as solid cattle waste and mixtures of solid and liquid cattle waste. The additional benefits exceed the additional expenses. Therefore, thermobarical pretreatment of such material will increase the net energy yield, reduce greenhouse gas emissions and have short to very short economic amortization periods. Thermobarical treatment of liquid cattle waste – a feedstock with low organic matter content – does not provide sufficient advantages compared with untreated liquid cattle waste. Therefore, substituting maize silage with treated liquid cattle waste is not recommended.

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Appendix

A1: Abbreviations

a	Year
AHO	Annual hours of operation
ADF	Acid detergent fiber
ADL	Acid detergent lignin
ADO	Annual days of operation
CBU	Cellobiase units
CHP	Combined heat and power unit
CMC	CO_2 mitigation costs
CO_2-eq.	CO_2-equivalent
ct	€-Cent
d	Day
DM	Dry matter
ECAM	Economic amortization mass
ECAP	Economic amortization period
EGU	Endoglucanase units
EPBM	Energy payback mass
EPBT	Energy payback time
FM	Fresh matter
GC-MS	Gas chromatography mass spectrometry
GHG	Greenhouse gas
GPBM	Greenhouse gas payback mass
GPBT	Greenhouse gas payback time
h	Hour
kJ	Kilojoule
kWh	Kilowatt hour
LCA	Life cycle assessment
LCM	Liquid cattle manure
LHV	Lower heating value
l_N	Normliter
NDF	Neutral detergent fiber
NMMO	N-methylmorpholine-N-oxide
ODM	Organic dry matter
OLR	Organic loading rate
OM	Organic matter
P1	Plant 1
P2	Plant 2
P[n]Y[n]M	Period in years and months
rpm	Revolutions per minute
SCM	Solid cattle manure
SCMW	Solid cattle manure and water
SLCM	Solid and liquid cattle manure
t	Ton
TBH	Thermobarical hydrolysis
T	Temperature

VOA	Volatile organic acids
w/o	Without
w/v	Weight/volume
w/w	Weight/weight

A2: Symbols in equations

equation number	symbol	nomenclature
1	$\dot{V}_{FM,MS}$	fresh matter volume-flow of maize silage substituted ($m^3 \cdot d^{-1}$)
	$\dot{V}_{FS}$	fresh matter volume flow of feedstock ($m^3 \cdot d^{-1}$)
	$Y_{CH4,FM,FS}$	methane yield of feedstock on a fresh matter basis (l_N $CH_4 \cdot kg^{-1}$ FM)
	$Y_{CH4,FM,MS}$	methane yield of maize silage on a fresh matter basis (l_N $CH_4 \cdot kg^{-1}$ FM)
	ρ_{FS}	bulk density of feedstock ($kg \cdot m^{-3}$)
	ρ_{MS}	bulk density of maize silage ($kg \cdot m^{-3}$)
2	$P_{th,FS}$	thermal input to feedstock for reaching set-point temperature ($kWh \cdot a^{-1}$)
	$\dot{m}_{FS}$	mass flow of the respective feedstock (kg FM$\cdot s^{-1}$)
	$c_{p,H2O}$	(temperature-independent) specific heat capacity of water ($kJ \cdot kg^{-1} \cdot K^{-1}$)
	$T_{set\text{-}point}$	set-point temperature of the pretreatment (°C)
	T_{FS}	feedstock temperature (°C)
	AHO	annual hours of operation ($h \cdot a^{-1}$)
3	$e_{th,FS}$	thermal input to feedstock for reaching set-point temperature ($kWh \cdot Mg^{-1}$ FM)
	$c_{p,H2O}$	(temperature-independent) specific heat capacity of water ($kJ \cdot kg^{-1} \cdot K^{-1}$)
	$T_{set\text{-}point}$	set-point temperature of the pretreatment (°C)
	T_{FS}	feedstock temperature (°C)
4	$P_{th,process}$	thermal input serving as process energy for the biogas plant ($kWh \cdot a^{-1}$)
	$\dot{m}_{FS}$	mass flow of the respective feedstock (kg FM$\cdot s^{-1}$)
	$c_{p,H2O}$	(temperature-independent) specific heat capacity of water ($kJ \cdot kg^{-1} \cdot K^{-1}$)
	$T_{set\text{-}point}$	set-point temperature of the pretreatment (°C)
	T_{dig}	temperature of digester content (°C)
	AHO	annual hours of operation ($h \cdot a^{-1}$)
5	$e_{th,process}$	thermal input serving as process energy for the biogas plant ($kWh \cdot Mg^{-1}$ FM)
	$c_{p,H2O}$	(temperature-independent) specific heat capacity of water ($kJ \cdot kg^{-1} \cdot K^{-1}$)
	$T_{set\text{-}point}$	set-point temperature of the pretreatment (°C)
	T_{dig}	temperature of digester content (°C)
6	$Y_{CH4,FM,LCM}$	methane yield of LCM assigned to the TBH on a fresh matter basis (l_N $CH_4 \cdot kg^{-1}$ FM)
	$w_{OM,LCM}$	mass fraction of organic matter in fresh matter of LCM
	$Y_{30,LCM,T}$	methane yield of LCM pretreated at the respective temperature T ($l_N \cdot kg^{-1}$ OM)
	$Y_{30,LCM,w/o}$	methane yield of untreated LCM ($l_N \cdot kg^{-1}$ OM)

equation number	symbol	nomenclature
7	$Y_{CH4,FM,SCM}$	methane yield of SCM on a fresh matter basis (l_N CH_4·kg^{-1} FM)
	$w_{OM,SCM}$	mass fraction of organic matter to fresh matter of SCM
	$Y_{30,SCM,T}$	methane yield of SCM pretreated at the respective temperature T (l_N·kg^{-1} OM)
8	$w_{CH4,FM,SCM,T}$	ratio of methane from SCM to methane from LCM within SLCM at the different pretreatment temperatures T
	$w_{FM,SCM}$	fresh matter mass fraction of SCM in SLCM
	$Y_{30,SCM,T}$	methane yield of SCM pretreated at the respective temperature T (l_N·kg^{-1} OM)
	$w_{OM,SCM}$	mass fraction of organic matter to fresh matter of SCM
	$Y_{30,LCM,T}$	methane yield of LCM pretreated at the respective temperature T (l_N·kg^{-1} OM)
	$w_{OM,LCM}$	mass fraction of organic matter in fresh matter of LCM
9	$Y_{CH4,FM,(S)LCM}$	methane from LCM within SLCM (l_N·kg^{-1} FM)
	$w_{CH4,FM,SCM,T}$	ratio of methane from SCM to methane from LCM within SLCM at the different pretreatment temperatures T
	$Y_{30,SLCM,T}$	methane yield of SLCM (l_N·kg^{-1} OM)
	$w_{CH4,FM,SCM,w/o}$	weighted ratio of the respective methane yields of untreated feedstock
	$Y_{30,SLCM,w/o}$	methane yield of untreated SLCM (l_N·kg^{-1} OM)
	$w_{OM,SLCM}$	mass fraction of organic matter in fresh matter of SLCM
10	$Y_{CH4,FM,S(L)CM}$	methane from SCM within SLCM (l_N·kg^{-1} FM)
	$w_{CH4,FM,SCM,T}$	ratio of methane from SCM to methane from LCM within SLCM at the different pretreatment temperatures T
	$Y_{30,SLCM,T}$	methane yield of SLCM (l_N·kg^{-1} OM)
	$w_{OM,SLCM}$	mass fraction of organic matter in fresh matter of SLCM
11	P_{MC}	methanation capacity (kWh·a^{-1})
	$Y_{CH4,FM,FS}$	methane yield of feedstock on a fresh matter basis (l_N CH_4·kg^{-1} FM)
	ρ_{CH4}	density of methane (kg·m^{-3})
	LHV_{CH4}	lower heating value of methane (MJ·kg^{-1})
	$\dot{m}_{FS}$	mass flow of the respective feedstock (kg FM·s^{-1})
	AHO	annual hours of operation (h·a^{-1})
12	e_{MC}	methanation capacity (kWh·Mg^{-1} FM)
	$Y_{CH4,FM,FS}$	methane yield of feedstock on a fresh matter basis (l_N CH_4·kg^{-1} FM)
	ρ_{CH4}	density of methane (kg·m^{-3})
	LHV_{CH4}	lower heating value of methane (MJ·kg^{-1})
13	$EPBT$	energy payback time (P[n]Y[n]M)
	E_{constr}	energy needed for construction materials (kWh)
	$P_{el,out}$	electric energy output (kWh·a^{-1})
	$P_{el,in}$	electricity input for operation of the TBH device (kWh·a^{-1})

equation number	symbol	nomenclature
14	$EPBM$	energy payback mass (Mg FM)
	E_{constr}	energy needed for construction materials (kWh)
	$e_{el,out}$	electric energy output (kWh·Mg^{-1} FM)
	$e_{el,in}$	electricity input for operation of the TBH device (kWh·Mg^{-1} FM)
15	GHG_{net}	net GHG balance (kg CO_2-eq.·kWh$_{el}^{-1}$)
	GHG_{constr}	emissions from TBH construction (kg CO_2-eq.·kWh$_{el}^{-1}$)
	$GHG_{el,in}$	emissions from TBH operation, (kg CO_2-eq.·kWh$_{el}^{-1}$)
	δGHG_{SCM}	emissions from SCM storage (kg CO_2-eq.·kWh$_{el}^{-1}$)
	δGHG_{MS}	emissions from maize supply (kg CO_2-eq.·kWh$_{el}^{-1}$)
16	$GHG_{net}^{\ddagger}$	net GHG balance (kg CO_2-eq.·Mg^{-1} FM)
	$GHG_{constr}^{\ddagger}$	emissions from TBH construction (kg CO_2-eq.·Mg^{-1} FM)
	$GHG_{el,in}^{\ddagger}$	emissions from TBH operation, (kg CO_2-eq.·Mg^{-1} FM)
	$\delta GHG_{SCM}^{\ddagger}$	emissions from SCM storage (kg CO_2-eq.·Mg^{-1} FM)
	$\delta GHG_{MS}^{\ddagger}$	emissions from maize supply (kg CO_2-eq.·Mg^{-1} FM)
17	$GHG_{el,in}$	emissions from TBH operation, (kg CO_2-eq.·kWh$_{el}^{-1}$)
	$P_{el,in}$	electricity input for operation of the TBH device (kWh·a^{-1})
	GHG_{grid}	emissions balance of grid electricity (kg CO_2-eq.· kWh$_{el}^{-1}$)
	$P_{el,out}$	electric energy output (kWh·a^{-1})
18	$GHG_{el,in}^{\ddagger}$	emissions from TBH operation, (kg CO_2-eq.·Mg^{-1} FM)
	$e_{el,in}$	electricity input for operation of the TBH device (kWh·Mg^{-1} FM)
	GHG_{grid}	emissions balance of grid electricity (kg CO_2-eq.· kWh$_{el}^{-1}$)
19	δGHG_{SCM}	emissions from SCM storage (kg CO_2-eq.·kWh$_{el}^{-1}$)
	M_{CO2}	molar mass of CO_2 (g·mol^{-1})
	$\dot{m}_{CH4,SCM}$	mass flow of methane attained from SCM (kg·s^{-1})
	M_{CH4}	molar mass of CH_4 (g·mol^{-1})
	$P_{el,out}$	electric energy output (kWh·a^{-1})
20	$\delta GHG_{SCM}^{\ddagger}$	emissions from SCM storage (kg CO_2-eq.·Mg^{-1} FM)
	M_{CO2}	molar mass of CO_2 (g·mol^{-1})
	M_{CH4}	molar mass of CH_4 (g·mol^{-1})
	$Y_{CH4,FM,SCM}$	methane yield of SCM on a fresh matter basis (l_N CH_4·kg^{-1} FM)
	ρ_{CH4}	density of methane (kg·m^{-3})
21	$\delta C_{MS}^{\ddagger}$	costs of electricity production using maize silage (€·Mg^{-1} FM)
	δC_{MS}	costs of electricity production using maize silage (ct·kWh$_{el}^{-1}$)
	$e_{el,out}$	electric energy output (kWh·Mg^{-1} FM)

equation number	symbol	nomenclature
22	$Profit$	profit (ct·kWh$_{el}^{-1}$)
	C_{constr}	costs of purchasing the TBH device (ct·kWh$_{el}^{-1}$)
	$C_{el,in}$	costs of electricity consumption of the TBH device (ct·kWh$_{el}^{-1}$)
	C_{MT}	costs of maintaining the TBH device (ct·kWh$_{el}^{-1}$)
	δC_{WL}	costs of wheel loader employment (ct·kWh$_{el}^{-1}$)
	$\delta C_{spreading}$	costs of changes in spreading-procedure (ct·kWh$_{el}^{-1}$)
	$\delta C_{el,out}$	revenues from a bonus within German feed-in tariff structure of electricity sales (ct·kWh$_{el}^{-1}$)
	δC_{MS}	costs of electricity production using maize silage (ct·kWh$_{el}^{-1}$)
23	$Profit^{\ddagger}$	profit (€·Mg^{-1} FM)
	$C_{constr}^{\ddagger}$	costs of purchasing the TBH device (€·Mg^{-1} FM)
	$C_{el,in}^{\ddagger}$	costs of electricity consumption of the TBH device (€·Mg^{-1} FM)
	$C_{MT}^{\ddagger}$	costs of maintaining the TBH device (€·Mg^{-1} FM)
	$\delta C_{WL}^{\ddagger}$	costs of wheel loader employment (€·Mg^{-1} FM)
	$\delta C_{spreading}^{\ddagger}$	costs of changes in spreading-procedure (€·Mg^{-1} FM)
	$\delta C_{el,out}^{\ddagger}$	revenues from a bonus within German feed-in tariff structure of electricity sales (€·Mg^{-1} FM)
	$\delta C_{MS}^{\ddagger}$	costs of electricity production using maize silage (€·Mg^{-1} FM)
24	$\delta C_{spr,dig,FS}$	costs of spreading digestate from the respective feedstock (ct·kWh$_{el}^{-1}$)
	$\dot{V}_{FM,FS}$	fresh matter volume flow of the respective feedstock (m^3·d^{-1})
	ρ_{FS}	bulk density of feedstock (kg·m^{-3})
	ρ_{dig}	density of digestate (kg·m^{-3})
	$C_{spr,V}$	costs of transport and spreading of LCM or digestate (ct·m^{-3})
	ADO	annual days of operation (d·a^{-1})
	$P_{el,out}$	electric energy output (kWh·a^{-1})
25	$\delta C_{spr,dig,FS}^{\ddagger}$	costs of spreading digestate from the respective feedstock (€·Mg^{-1} FM)
	$\dot{V}_{FM,FS}$	fresh matter volume flow of the respective feedstock (m^3·d^{-1})
	ρ_{FS}	bulk density of feedstock (kg·m^{-3})
	ρ_{dig}	density of digestate (kg·m^{-3})
	$C_{spr,V}$	costs of transport and spreading of LCM or digestate (ct·m^{-3})
	$\dot{m}_{FS}$	mass flow of the respective feedstock (kg FM·s^{-1})
26	$\delta C_{spr,SCM,w/o}$	costs of spreading untreated SCM (ct·kWh$_{el}^{-1}$)
	$\dot{V}_{FM,SCM}$	fresh matter volume flow of SCM (m^3·d^{-1})
	ρ_{SCM}	bulk density of SCM (kg·m^{-3})
	$C_{spr,m}$	costs of transport and spreading of SCM (ct·Mg^{-1})
	ADO	annual days of operation (d·a^{-1})
	$P_{el,out}$	electric energy output (kWh·a^{-1})

equation number	symbol	nomenclature
27	$\delta C^{\neq}_{spr,SCM,w/o}$	costs of spreading untreated SCM (€·Mg^{-1} FM)
	$C_{spr,m}$	costs of transport and spreading of SCM (ct·Mg^{-1})
28	$\delta C_{spreading}$	costs of changes in spreading-procedure (ct·kWh$_{el}^{-1}$)
	$\delta C_{spr,SCM,w/o}$	costs of spreading untreated SCM (ct·kWh$_{el}^{-1}$)
	$\delta C_{spr,dig,SCM}$	costs of spreading digestate from SCM (ct·kWh$_{el}^{-1}$)
	$\delta C_{spr,dig,MS}$	costs of spreading digestate from maize silage (ct·kWh$_{el}^{-1}$)
29	$\delta C^{\neq}_{spreading}$	costs of changes in spreading-procedure (€·Mg^{-1} FM)
	$\delta C^{\neq}_{spr,SCM,w/o}$	costs of spreading untreated SCM (€·Mg^{-1} FM)
	$\delta C^{\neq}_{spr,dig,SCM}$	costs of spreading digestate from SCM (€·Mg^{-1} FM)
	$\delta C^{\neq}_{spr,dig,MS}$	costs of spreading digestate from maize silage (€·Mg^{-1} FM)
30	$\delta C^{\neq}_{el,out}$	revenues from a bonus within German feed-in tariff structure of electricity sales (€·Mg^{-1} FM)
	$e_{el,out}$	electric energy output (kWh·Mg^{-1} FM)
31	$ECAP$	economic amortization period (P[n]Y[n]M)
	$Investment$	investment (€)
	$Profit$	profit (ct·kWh$_{el}^{-1}$)
	$Depreciation$	depreciation (€·a^{-1})
	$Interest$	interest rate (€·a^{-1})
32	$ECAM$	economic amortization mass (t FM)
	$ECAP$	economic amortization period (P[n]Y[n]M)
	$\dot{m}_{FS}$	mass flow of the respective feedstock (kg FM·s^{-1})
	ADO	annual days of operation (d·a^{-1})
33	CMC	CO_2 mitigation costs (€·Mg^{-1} CO_2-eq.)
	$C_{EP,TBH}$	electricity production costs (€·kWh$_{el}^{-1}$)
	$C_{EP,grid}$	grid electricity-mix production costs (€·kWh$_{el}^{-1}$)
	GHG_{grid}	emissions balance of grid electricity (kg CO_2-eq.· kWh$_{el}^{-1}$)
	GHG_{net}	net GHG balance (kg CO_2-eq.·kWh$_{el}^{-1}$)
34	$Y_{30,T}$	predicted methane yield of treated feedstock after 30 days (l_N CH_4·kg^{-1} OM)
	$Y_{30,w/o}$	methane yields of untreated feedstock after 30 days (l_N CH_4·kg^{-1} OM)
	$Y_{IP,w/o}$	methane yields of untreated feedstock at inflection point (l_N CH_4·kg^{-1} OM)
	$k_{IP,T}$	average formation rate of treated feedstock until inflection point (l_N CH_4·kg^{-1} OM·d^{-1})
	$k_{IP,w/o}$	average formation rate of untreated feedstock until inflection point (l_N CH_4·kg^{-1} OM·d^{-1})

equation number	symbol	nomenclature
35	$K(T)$	ratio of average formation rate of treated feedstock until inflection point to untreated feedstock until inflection point
	K_0	ratio of the average formation rates up to the inflection point of untreated feedstock

A3: List of figures

A4: List of tables